Naphthocyclobutenes and Benzodicyclobutadienes: Synthesis in the Solid State and Anomalies in the Bond Lengths

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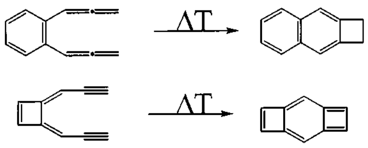
The title four-membered ring compounds, naphthocyclobutenes and benzodicyclobutadienes, were produced by thermal cyclization reaction of crystalline 1,2-diallenylbenzenes and 1,6-diethynyldiallenes, respectively. These solid-state reactions proceeded efficiently and stereoselectively. The naphthocyclobutenes were shown to have extremely long $C_{(sp^3)}-C_{(sp^3)}$ bonds (1.720–1.733 Å). The benzodicyclobutadienes were also shown to have extremely long $C_{(sp^2)}-C_{(sp^2)}$ bonds (1.540 Å).

1. Introduction

It has been well established that thermal and photochemical organic reactions proceed efficiently in the solid state.[1] In many cases, organic reactions proceed much faster in the solid state than in solution. Moreover, solid-state reactions occur selectively because molecules in the crystal are arranged regularly.

Recently, the thermal cyclization reaction of diallenes to cyclobutene derivatives, and of diacetylenes to cyclobutadiene derivatives, was found to proceed stereoselectively in the solid state. These reactions can be monitored by measurement of IR and UV spectra in the solid state. By combining these spectral data with X-ray analytical data, the reaction mechanism in the solid state can be clarified. These results show that the movement of molecules in the crystal is quite easy. Some of this dynamic behavior of molecules in the crystal is described.

During the course of the structural study of the four-membered ring compounds produced by the solid-state cyclization reactions of diallenes and diacetylenes, some anomaly in their bond length was found. Naphthocyclobutene derivatives were disclosed to have extremely long C–C bonds (1.720–1.730 Å). As far as we are aware, these are the longest known C–C bonds. The reasons for this are discussed. On the other hand, benzodicyclobutadiene derivatives are constructed from a deformed benzene ring which has an extremely long C–C bond (1.540 Å). This bond length corresponds to a C–C single bond. These data show that the six-membered ring in the benzodicyclobutadiene is no longer benzene. The structures of these compounds are discussed.



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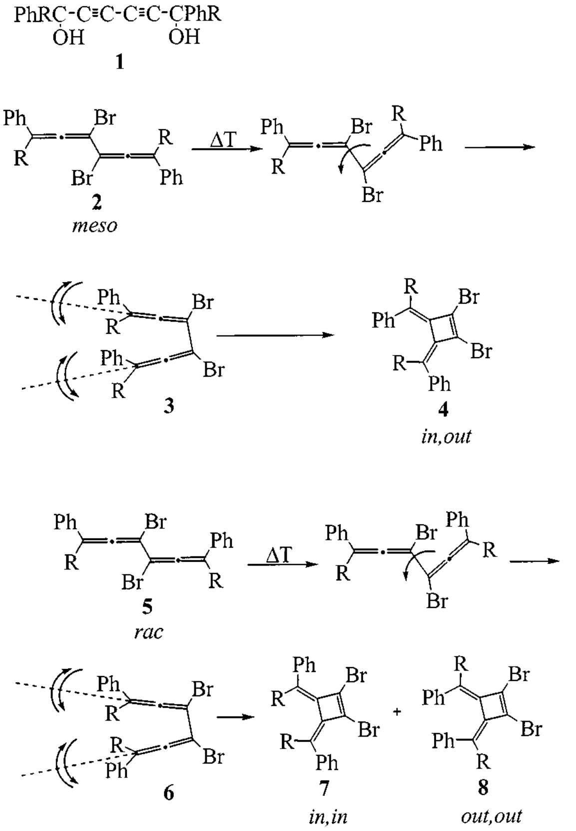
2. Thermal Cyclization of Diallenes in the Solid State

No thermally irreversible unimolecular reactions from crystal to crystal had been reported until 1998, although reversible reactions such as thermochromism and single-crystal-to-single-crystal thermal conversion of a cyclic photodimer of a styrylpyrylium derivative to its monomer[2] were known. Recently, it was found that heating of crystalline diallene derivatives in the solid state gives four-membered ring compounds through crystal-to-crystal thermal cyclization in quantitative yields.

2.1. Stereoselective Thermal Conversion of *s-trans*-Diallene into Dimethylenecyclobutene via the *s-cis*-Diallene in the Crystalline State

The thermal cyclization in solution of 3,4-dibromo-1,1,6,6-tetraphenyl-1,2,4,5-hexatetraene **(2a)** to 1,2-dibromo-3,4-bis(diphenylmethylene)cyclobutene **(4a)**,[3] and of unsubstituted and alkyl-substituted derivatives to the corresponding dimethylenecyclobutenes,[4] has been reported. The thermal conversion of **2a** to **4a** was also found to occur in the crystalline state.[5] Heating a colorless crystal of **2a**, prepared from 1,1,6,6-tetraphenyl-2,4-hexadiyne-1,6-diol **(1a)** and aqueous HBr according to the reported method,[6] at 150 °C gave **4a** in quantitative yield.[5] Since no liquid state was observed during the conversion of **2a** to **4a**, the reaction in the crystal is a real solid-state reaction. An X-ray analysis showed that molecules of **2a** have an *s-trans* conformation in the crystal. This structure is reasonable because even 1,2,4,5-hexatetraene exists in an *s-trans* form both as a gas[7] and in solution.[8] In order to cyclize to **4a**, **2a** should first isomerize to its *s-cis* isomer **3a** in the crystal. The conformational change of **2a** to **3a** requires a rotation of the sterically bulky 1,1-diphenylallene moiety around the single bond connecting the two allene groups in the crystalline state, as indicated in Scheme 1. A similar conformational change of *s-trans*-diallene to *s-cis*-diallene in solution, followed by the addition of SO_2 to give a cyclic sulfone derivative has been discussed.[9] Furthermore, thermal conversion of the *s-cis*-diallene **3a** to **4a** should also be accompanied by a molecular motion of the 1,1-diphenylmethylene groups. This dynamic behavior of the molecules in the crystalline state is very interesting. To verify whether the rearrangement of *s-trans*-diallene to *s-cis*-diallene and the cyclization of the latter to dimethylenecyclobutene proceed stereoselectively, the thermal reactions of *meso*- (**2b**) and *rac-s-trans*-1,6-diphenyl-1,6-bis(*p*-tolyl)-3,4-dibromo-1,2,4,5-hexatetraene (**5b**) were studied.

The reaction of a mixture of *meso*- and *rac*-1,6-diphenyl-1,6-bis(*p*-tolyl)-2,4-hexadiyne-1,6-diol (**1b**) with aqueous HBr gave a mixture of **2b** and **5b** which, upon fractional recrystallization, gave pure **2b** and **5b** as colorless crystals. The *s-trans* structures of these were elucidated by X-ray analysis.[5] Heating crystals of **2b** at 135 °C gave the *in,out* isomer **4b**, while heating **5b** at 145 °C gave a 1:1 mixture of the *in,in* isomer **7b** and the *out,out*-3,4-bis(phenyl-*p*-tolylmethylene)-1,2-dibromocyclobutene (**8b**) in quantitative yields. The structures of all the products were elucidated by X-ray analysis.[5]



Scheme 1. Stereoselective thermal conversion of *s-trans*-diallenes into dimethylenecyclobutenes via *s-cis*-diallenes in crystals; **a**: R = Ph; **b**: R = *p*-MeC_6H_4

Since the thermal reaction of **2b** and **5b** in boiling xylene gave the same products, the steric course of the solid-state reaction which is shown in Scheme 1 should be the same as that in solution. Compounds **2b** and **5b** rearrange first to **2b** and **6b**, respectively, and their conrotatory [2+2] ring closure gives **4b** and a 1:1 mixture of **7b** and **8b**, respectively. Mechanistic studies of the thermal conversion of diallene to dimethylenecyclobutene in solution and in the gas phase have revealed that the reaction proceeds through an electrocyclic conrotatory process.[10]

To verify that these reactions occur in the solid state and not in the liquid state, the thermal reaction of **5b** in the crystal was studied by taking DSC data and IR spectra,and by monitoring the course of the reaction through a microscope. In the DSC diagram, **5b** revealed a peak for an exothermic reaction at around 150 °C, which is attributable to the rearrangement of **5b** to **6b**, followed by cyclization to a mixture of **7b** and **8b**, plus a peak for an endothermic conversion at around 193 °C, which is attributable to the melting point of the product (Figure 1).

This assignment is reasonable, since a 1:1 mixture of **7b** and **8b** showed a peak for an endothermic process at 194 °C in the DSC measurement. On the other hand, **2b** showed a peak for an exothermic conversion at around 178 °C and

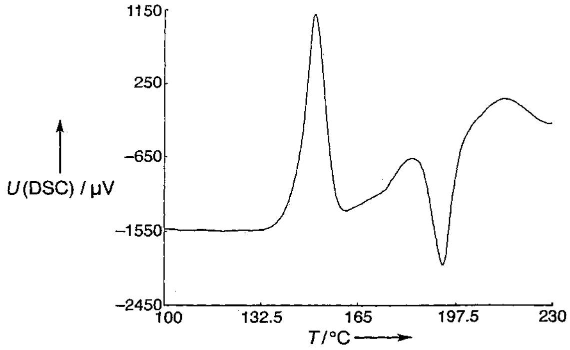


Figure 1. DSC diagram of **5b**

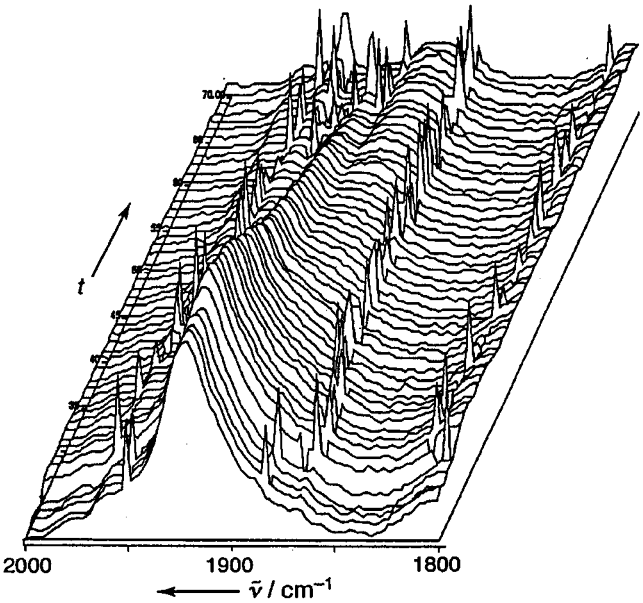
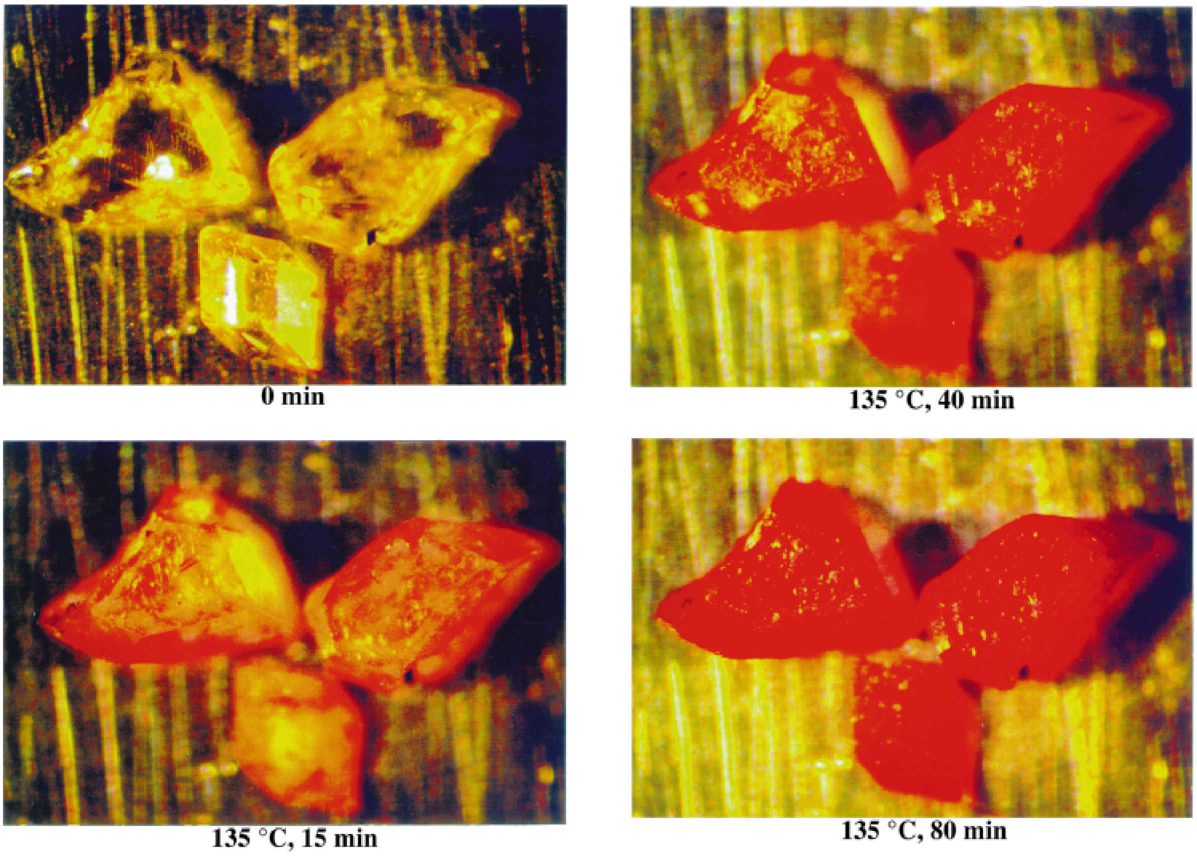


Figure 2. IR spectra showing the thermal reaction of **5b** in the crystalline state at 125 °C; the spectrum was measured every minute for 50 min

a peak for an endothermic conversion at 216 °C that is attributable to the melting point of **4b** (m.p. 214–215 °C). When the IR spectrum of a single crystal of **5b** was measured continuously every minute for 50 min at 125 °C, the signal at $\tilde{\nu} = 1927\ \mathrm{cm^{-1}}$ (C=C=C) gradually decreased and finally disappeared (Figure 2).

By heating **5b** in the crystalline state at 135 °C on a hot plate for 80 min, it was completely converted into **7b** and **8b** without melting. This crystal-to-crystal conversion was monitored through a microscope, and a molten state was not observed during the reaction, although the reaction product was no longer a single crystal (Figure 3).

These findings clearly support the proposal that the conversion of the *s-trans*-diallene into dimethylenecyclobutene via the *s-cis*-diallene really occurs in the crystalline state and not in the molten state. They also verify that the molecular motion of the sterically bulky 1,1-diarylallene group in the rearrangement of the *s-trans*-diallene into its *s-cis* iso-



0 min

135 °C, 40 min

135 °C, 15 min

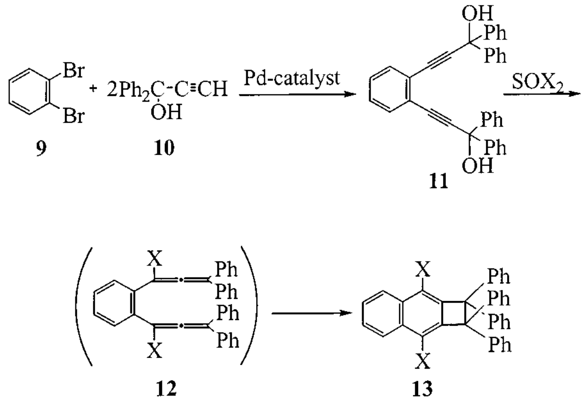
135 °C, 80 min

Figure 3. Crystal-to-crystal conversion of **5b** into **7b** and **8b**

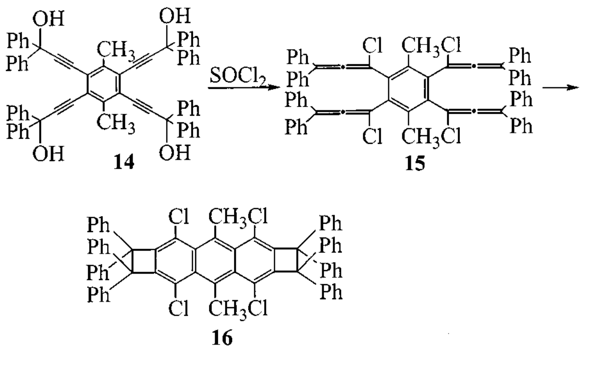
mer, and that of the 1,1-diarylmethylene group in the cyclization of *s-cis*-diallene to dimethylenecyclobutene occur in the crystal.

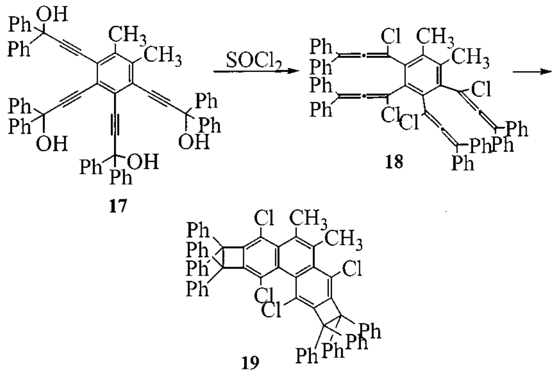
2.2. Thermal Conversion of 1,2-Diallenylbenzenes into Naphthocyclobutenes

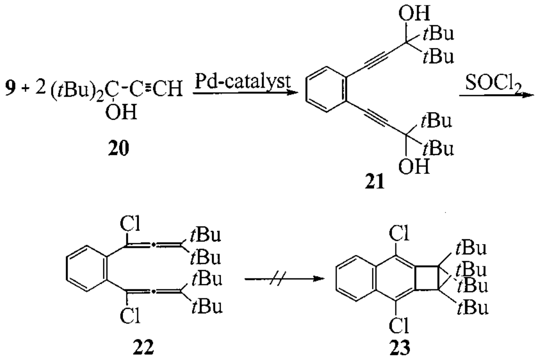
Although 1,2-dihydrocyclobutaarenes such as benzocyclobutene, naphthocyclobutene and anthrodicyclobutene have long been considered interesting from the point of view of structural[11] and synthetic chemistry,[12] preparation of these compounds is not easy.[13] Recently, a new synthetic route to these 1,2-dihydrocyclobutaarenes through the thermal cyclization reaction of 1,2-diallenylarenes derived from a 1,2-diynediol by a propargyl rearrangement has been developed.[14] Reaction of 1,2-dibromobenzene (**9**) with 1,1-diphenyl-2-proyn-1-ol (**10**) in the presence of a Pd-catalyst[15] gives the 1,2-diynediol derivative **11**. Treatment of **11** with thionylhalide according to the reported method[3,16] gives the 1,2-diallenylbenzene derivative **12**, which immediately cyclizes to give naphthocyclobutene (**13**) as colorless crystals. Although **12** was too reactive to isolate, the 1,2,4,5-tetraallenyl derivative **15**, formed from the 1,2,4,5-tetraynetetraol **14**, was isolated in a pure state as colorless prisms. By heating a crystal of **15** in the solid state, the anthrodicyclobutene derivative **16** was obtained as yellow prisms. However, 1,2,3,4-tetraallenylbenzene (**18**) derived from the 1,2,3,4-tetraynetetraol **17** was not isolated and gave the phenanthrodicyclobutene derivative (**19**) immediately by a cyclization process.[14]



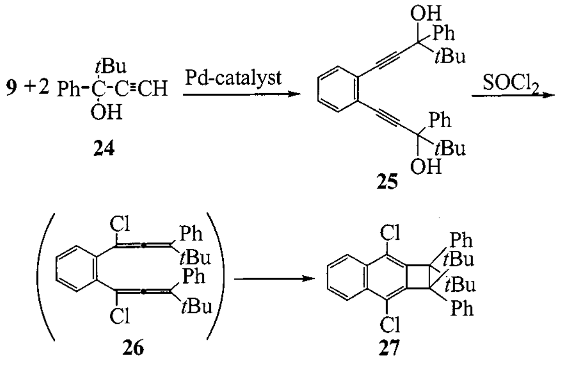
a : X=Cl; b : X=Br; c : X=I

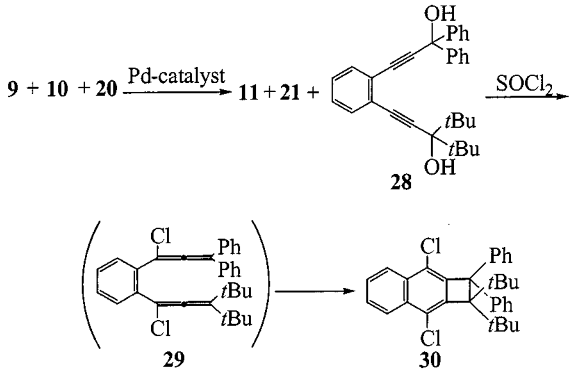






However, the 1,2-diallenylbenzene derivative **22** with four *t*Bu groups on its allene carbons, prepared by coupling **9** with 1,1-di-*tert*-butyl-2-propyn-1-ol (**20**) to give **21**, followed by its propargyl rearrangement, did not cyclize to the corresponding naphthocyclobutene **23**, probably because of

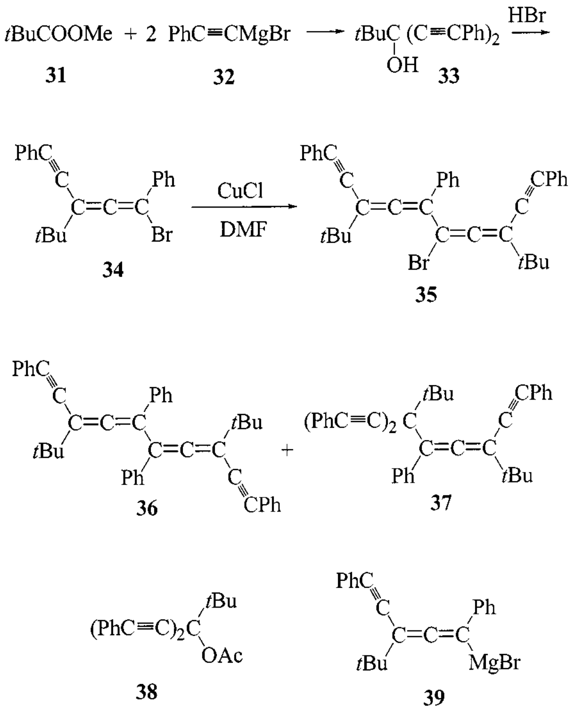




a serious steric crowding in **23**. Compound **22** exists as thermally stable colorless prisms which show a clear melting point at 158–159 °C and $\nu_{(C=C=C)}$ at 1920 cm^{-1}.[14] Contrarily, the propargyl rearrangement of the 1,2-diynediol derivative **25**, symmetrically substituted with two phenyl and two *t*Bu groups, prepared from **9** and **24** by the coupling reaction, gave the naphthocyclobutene **27** via the diallene intermediate **26**.[17] The *trans*-structure of **27** was elucidated by an X-ray analysis.[17] The unsymmetrically substituted naphthocyclobutene **30**, with two phenyl and two *t*Bu groups, was also prepared by the following method: the coupling reaction of **9** with **10** and **20** gave **11** (51%), **21** (5%) and **28** (24%). Treatment of **28** with $SOCl_2$ gave **30** via the corresponding diallene **29**.

2.3. Thermal Conversion of 1,6-Diethynyldiallenes into Benzodicyclobutadienes via 3,4-Bis(ethynylmethylene)-cyclobutenes

Reaction of the alcohol **33**, prepared from methyl pivalate (**31**) and (phenylethynyl)magnesium bromide (**32**), with HBr in AcOH gave the phenylethynylbromoallene **34**. Treat-



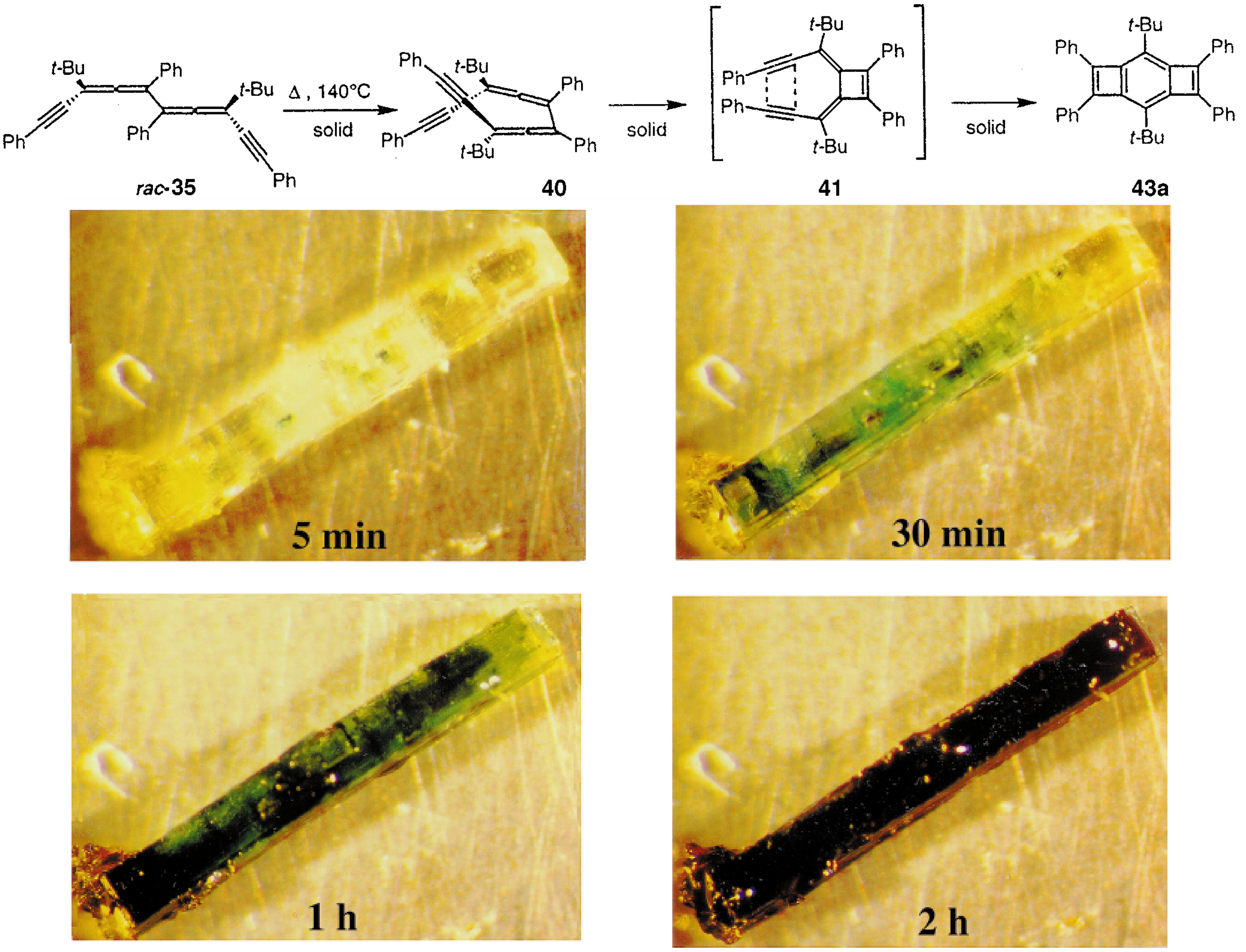
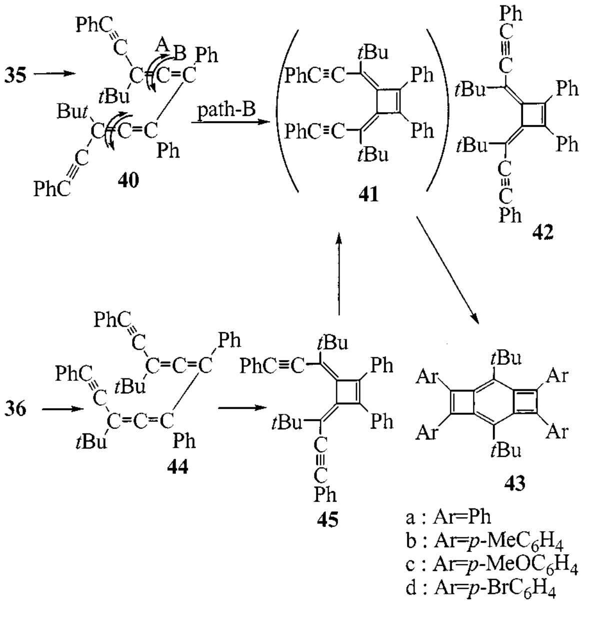


Figure 4. Crystal-to-crystal conversion of **35** into **43a**

ment of **34** with CuCl in DMF by a previously reported new allene coupling method[18] gave D,L- (**35**) and *meso*-3,8-di-*tert*-butyl-1,5,6,10-tetraphenyldeca-3,4,6,7-phenylethynylocta-3,4-diene-1,7-diyne (**36**) and compound **37**, in yields of 11, 11 and 54%, respectively.[19] The same compounds could also be obtained by CuCl treatment of the acetate **38** or the Grignard reagent **39**.[19]

When **36** was heated in benzene, benzodicyclobutadiene (**43a**) was produced as green needles in quantitative yield.[20] The reaction probably proceeds via the following steps: firstly, the *s*-*trans* structure in **36** turns to the *s*-*cis* structure **40**; secondly, conrotatory ring closure of **40** gives *in,in*-3,4-bis(phenylmethylene)cyclobutene (**41**), and thirdly, thermal reaction between the two acetylene moieties in **41** results in **43a**. In the thermal conversion of **40** into the dimethylenecyclobutene derivative, only the *in,in*-bis(phenylethynyl)-isomer **41** was produced by the conrotatory ring closure in the A direction; the *out,out*-bis(phenylethynyl)isomer **42** was not produced as serious steric repulsion between the two *t*Bu groups is expected in **42**. On the other hand, heating of **36** in benzene gave the *in,out*-bis(phenylethynyl) isomer **45** by a conrotatory ring closure of the *s*-*cis* diallene **44** produced by isomerization of **36**. Further heating of **45** in xylene gave **43a**. This reaction probably proceeds via **41**, which is initially produced by a thermal isomerization of **45**.[20]



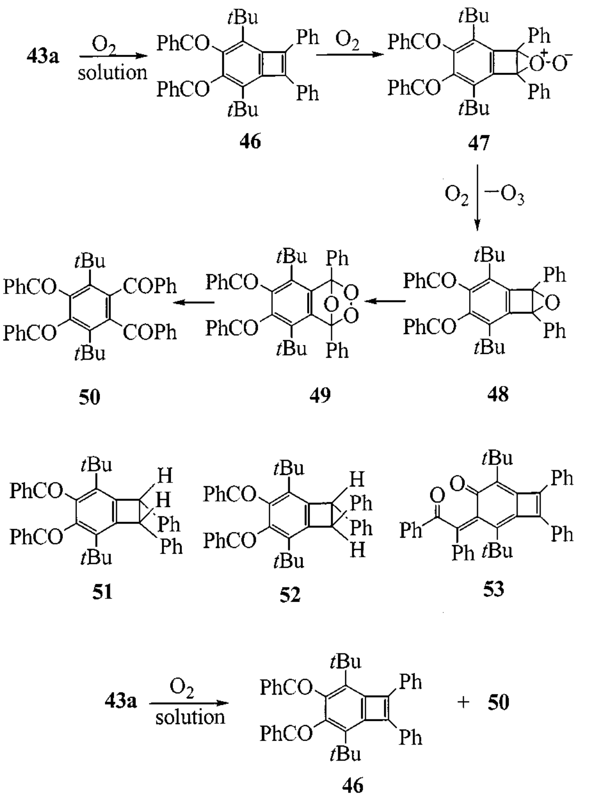
The thermal conversion of **35** into **43a** via **40** and **41** was observed even in the crystalline state. As shown in Figure 4, colorless crystals of **35** turn into green crystals of **43a** by gradually heating to 140 °C, and the reaction is completed within 2 h.

Since **35** has an *s*-*trans*-structure in its crystal,[21] isomerization of the *s*-*trans* configuration to the *s*-*cis* one should occur before the conrotatory ring closure. It is also interesting that these molecular motions with bulky substituents easily occur in the crystalline state.

By the same procedure, three derivatives **43a**, **43b**, **43c** and **43d**, were prepared by using *p*-methyl, *p*-methoxy and *p*-bromophenylethynylmagnesium bromide, respectively, instead of **32**.[22]

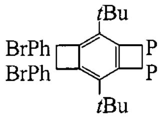
2.4. Synthesis of Benzocyclobutene Derivatives from Benzodicyclobutadienes

Oxidation of **43a** with molecular oxygen in solution gave dibenzoylcyclobutadiene oxide (**48**), which was further oxidized to its peroxide **49**, and finally to the tetrabenzoylbenzene derivative **50**. However, oxidation of **43a** with molecular oxygen in the solid state gave *o*-quinomethide **53**.



Stirring a suspension of **43a** in MeOH under an O_2 atmosphere at room temperature for 1 h afforded **48** in 96% yield.[23] The oxidation of **43a** to **48** proceeds via dibenzoylbenzocyclobutadiene (**46**) and its peroxide **47**.[23] Hydrogenation of **48** over Pd/C gave *cis*-dibenzoylbenzocyclobutane (**51**) in 46% yield. Contrarily, $NaBH_4$ reduction of **48** gave **51** and its *trans*-isomer **52** in 68 and 12% yield, respectively.[23] However, keeping crystals of **43a** at room temperature for 5 days afforded **53** in 50% yield together with **50** in 13% yield.[23]

Addition of Br_2 to **43a** gave the tetrabromide **54**, although its stereochemistry was not elucidated. This bromination also occurs in the solid state. Keeping a mixture of powdered **43a** and the crystalline bromine complex, $(nBu)_4N^+Br^-\cdot Br_2$, in N_2 for 3 h gave **54** in quantitative yield. This reaction can be monitored by the measurement of UV spectra in the solid state.



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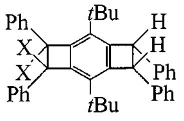

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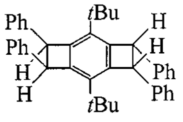

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a : X=Br
b : X=Cl

Addition of HBr and HCl to **43a** gave the *cis*, *trans*-addition products, **55a** and **55b**, respectively. However, reaction of **55a** with *n*BuLi gave the *cis*, *cis*-tetrahydro derivative **56**.

3. Anomalies in the Bond Lengths

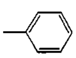
Some anomalies in the bond lengths were found for the four-membered ring compounds prepared in the previous sections from the X-ray analytical studies. One is an extremely long C–C bond of the cyclobutene ring (1.720–1.730 Å) contained in the naphtho-, anthro- and phenanthrocyclobutene derivatives. As far as we are aware, these are the longest C–C bonds which have been observed so far. The other anomaly is an extremely long C–C bond in a benzene ring (1.540 Å) in the benzodicyclobutadiene derivatives. This result shows that the six-membered ring is no longer aromatic. It is an interesting subject to study what kind of structure is available for these compounds.

3.1. History of The Study of Long C–C Bonds

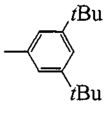
After Gomberg's famous discovery of the triphenylmethyl radical **58a**,[24] its dimer was believed to be hexaphenylethane (**57a**) for more than half a century until the correct structure was elucidated in 1968.[25] In 1978, hexakis(2,4-di-*tert*-butyl-4-biphenylyl)ethane (**57c**) was prepared as the first example of a hexaarylethane.[26] Theoretical calculations suggested that the central C–C bond length of both **57a**[27] and **57c**[28] is abnormally long at 1.64 Å. In 1986, the central C–C bond length of **57b** was found to be 1.67(3) Å by X-ray analysis.[28] The abnormally long central C–C bond in **57b** and **57c** has also been determined to lie between 1.64 and 1.65 Å by nutation NMR spectroscopy.[29]

$$\underset{\mathbf{57}}{Ar_3C\text{-}CAr_3} \rightleftharpoons \underset{\mathbf{58}}{2Ar_3C\bullet}$$

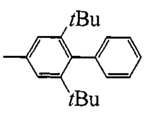
a : Ar=



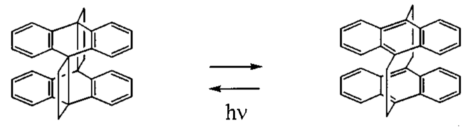
b : Ar=



c : Ar=



Numerous other efforts have been directed at finding much longer C–C bonds. In 1966, the C–C bond of the four-membered ring in the photoirradiation product **59** of the cyclophane **60** was reported to be 1.77 Å.[30] However, theoretical calculations did not support the data.[31] Finally, the extremely long bond in **59** was found to be an error. An X-ray analysis was performed for a mixture of **59** and **60** which had formed in a topotactic reaction.[32] A nutation diffraction analysis of **59** showed that the central C–C bond length is actually 1.64(1) Å.[31] This is in perfect agreement with the calculated value of 1.64 Å.[31] X-ray analytical reinvestigations of **59** by two further research groups measured the central bond length at 1.663(4)[33] and 1.648(3) Å.[34]



59 **60**

61 **62**

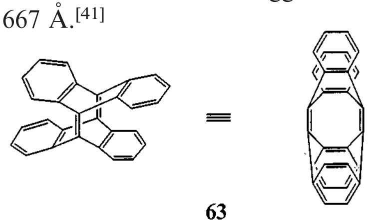
a : R=R'=Me
b : R=Me; R'=CN

Another error in the long C–C bond problem has happened for bisnorcaradienes (**61**). Although a very long central C–C bond was found for **61a** (1.826 Å) and **61b** (1.850 Å) by X-ray analysis,[35] these data were later found to be erroneous since the analysis was carried out with a sample contaminated with ring-opened annulene (**62**).[36]
The history of long C–C bonds was well documented by Kaupp in 1997.[37]

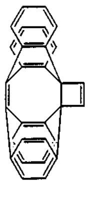
3.2. Extremely Long C–C Bonds in Naphtho- and Phenanthrocyclobutene Derivatives

Unequivocal overlong C–C bonds have been found in the cyclobutene ring of **13a** (1.720 Å) and **19** (1.724 Å).[38] In the hexaarylethane **57**, six aryl groups can be arranged in sterically less-crowded positions by twisting around the central bond. The twisted structure has been elucidated for **57b** by an X-ray analysis.[28] Because of this twisted structure, the steric repulsion among the aryl groups in **57** is relaxed and thus the central C–C bond is not very extended. In **13a** and **19**, however, four phenyl groups binding to a more planar and rigid benzocyclobutene ring are forced to stay in sterically much more crowded positions. According to the steric repulsion, the $C_{(sp^3)}-C_{(sp^3)}$ bond would be extremely extended in **13a** and **19**. To confirm the experimental bond length in **13a**, the X-ray crystal structure was determined by collecting data at low temperature (90 K). Refinement of this highly accurate data set converged on a C–C bond length of 1.710(2) Å, in excellent agreement with the value (1.720 Å) determined from the room temperature data.[39]

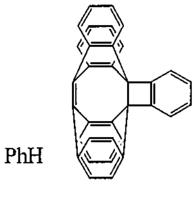
The $C_{(sp^3)}-C_{(sp^3)}$ bonds in the cyclobutene derivatives **64** [1.667(3) Å] and **65** [1.713(2) Å], obtained by the [2+2]cycloaddition of acetylene and benzyne, respectively, to tetradehydrodianthracene (**63**) are also extended.[40] Theoretical calculations of the bond length for **64** (1.671 Å) and **65** (1.703 Å) by the PM3 method support the experimental data.[40] The values calculated by the Becke 3LYP/6–31G* method for **64** (1.700 Å) and **65** (1.721 Å) are also comparable to those observed.[40] The latter calculation method is also applicable to **13a** and the resulting bond lengths of 1.710(5)–1.724(5) Å are comparable to those observed (1.720 Å).[39] The calculated value for **13a** with B3LYP/6–31G* is also in good agreement with the experimental data.[40] This calculation suggests that the long bond in **59** is 1.667 Å.[41]



63

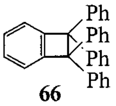


64

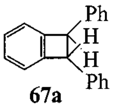


65

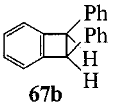
Computations [B3LYP/dz(2d,p)] on 1,1,2,2-tetraphenylbenzocyclobutene (**66**), which is a suitable model for **13a**, in a C_2 conformation similar to that found crystallographically for **13a** predict a bond length of 1.708 Å, in excellent agreement with the experimental observation for **13a**. Similar computations on **66** in a C_{2v} conformation predicted a still longer bond of 1.722 Å.[39]



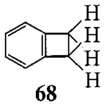
66



67a



67b



68

A search of the Cambridge Structural Database (CSD) uncovered that about 90 examples of $C_{(sp^3)}-C_{(sp^3)}$ benzocyclobutane bonds cluster about 1.58 ± 0.5 Å and do not exceed 1.63 Å.[39] The $C_{(sp^3)}-C_{(sp^3)}$ bonds in 1,2-dimethylenecyclobutane derivatives also do not exceed 1.65 Å.[44] What is the reason for these long bonds in **13a**? There are two main possible explanations. One is the steric repulsion among bulky substituents, and the other is a through-bond interaction.[42]

In order to study how the steric repulsion extends the C–C bond in **13a** the benzocyclobutene derivatives (**27**, **30**) substituted with *t*Bu groups were prepared as described in Section 2.2.[17] An X-ray structural study showed that the $C_{(sp^3)}-C_{(sp^3)}$ bond lengths of the cyclobutene ring in **27** and **30** are 1.686 and 1.729 Å, respectively.[17] These are again extremely long bonds, especially the bond in **30** which is the longest one observed so far. These results clearly show that the steric repulsion between the two *t*Bu and two phenyl groups in **27** and **30** is one of the most important reasons for the elongation of the C–C bond. This steric crowding is clearly shown in the X-ray results.[17]

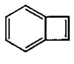
However, a through-bond interaction has also been postulated as being an important reason for the elongation of the C–C bond in **13a**.[43] Schleyer et al. calculated the C–C bond length in **13a** of C_2 symmetry using B3LYP/6–31G** to be 1.731 Å, which is in good agreement with the observed value (1.720 Å). They have interpreted the reason for the formation of this extremely long bond as being due to through-bond interaction effects.[43] In order to confirm whether the through-bond interaction is important or not in the elongation of C–C bonds, the molecular structures of **51** and **52**, which have *cis*- and *trans*-substituted diphenylcyclobutene rings, respectively, were studied by X-ray analysis.[45] The through-bond interaction is expected to be greater in **52** than in **51**. In **51**, more steric repulsion is expected than in **52**. X-ray analysis at room temperature and 90 K showed that **51** has a slightly longer C–C bond, 1.623 Å and 1.606 Å, respectively. Unfortunately, however, the C–C bond length in **52** could not be determined due to the presence of disorder. In these systems, however, no electronic interaction between the benzoyl groups and the benzocyclobutene ring occurs since the benzoyl moieties are located in a perpendicular position to each other.[45] The coupling constants at the cyclobutene ring in **51** (J_{CH} = 159 Hz) and **52** (146 Hz) are larger than that in benzocyclobutene (**68**) (138 Hz).[46]

The fact that the *cis*-1,2-diphenylbenzocyclobutene system does not have an extremely long C–C bond was confirmed by X-ray structural studies of **55a** and **55b**. The C–C bond lengths of the diphenylcyclobutene rings in **55a** [1.613(3) Å] and in **55b** [1.610(3) Å] are similar to that of **51**.[21] The C–C bond lengths of the dihalodiphenylcyclobutene rings in **55a** [1.620(3) Å] and **55b** [1.626(3) Å] are also not very anomalous in comparison to those in **13**, **27** and **30**.[21] However, the molecular structures of **54** and **56** have not yet been analyzed. Furthermore, the calculated values for *trans*-**67a** (1.598 Å) and *cis*-1,2-diphenylbenzocyclobutenes (**67b**) (1.636 Å) using B3LYP/dz (2d,p) suggest that steric factors are more important in extending the bond length than electronic factors.[39] This will be clarified by future structural studies of **67a** and **67b**.

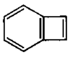
In conclusion, one of the most important reasons for the extremely long C–C bonds in benzocyclobutene derivatives is due to steric repulsion in the four-membered ring. However, the contribution of through-bond interactions cannot be completely ignored. X-ray analysis showed that the iododerivative of **13a** (**13c**) has a slightly longer C–C bond [1.733(6) Å] than that of **13a**.[45] However, the bromo-derivative **13b** has not yet been analyzed.

3.3. Extremely Long C–C Bonds in the Benzene Ring of Benzodicyclobutadiene Derivatives

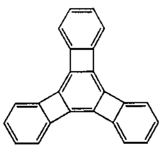
For benzocyclobutadiene (**69**) and tris(benzocyclobutadieno)benzene (**70**), the contribution of the structure which



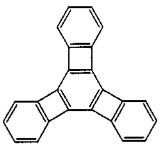
69a



69b



70a



70b

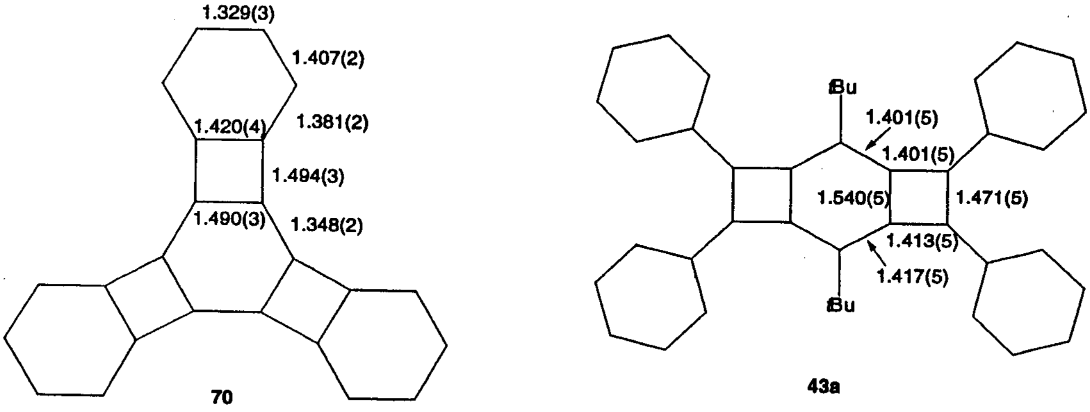
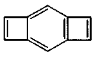
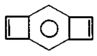


Figure 5. Bond lengths in **70** and **43a**

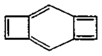
Table 1. Calculated (BL3LYP/6-31G* and MP2/6-31G*) geometries and relative energies of the two isomers of **71**



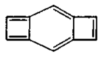
71



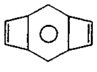
71a



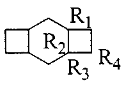
71b



71c



71d

	Isomer	Level	R_1	R_2	R_3	R_4	E /kcal mol^{-1}
	**71d**	BL3LYP/6-31G*	1.3888	1.5641	1.3916	1.4583	-2.4
	71a	BL3LYP/6-31G*	1.3944	1.4026	1.5430	1.3456	0
	71d	MP2/6-31G*	1.3989	1.5545	1.3921	1.4587	-3.7
	71a	MP2/6-31G*	1.3943	1.4082	1.5361	1.3456	00

contains the antiaromatic cyclobutadiene moiety **69b** and **70b**, respectively, would be unfavorable, although the dimethylenecyclobutene (**69a**) and radiallene structure (**70a**), respectively, should contribute more favorably. It has been confirmed by an ab initio calculation that **69b** is much higher in energy than **69a**.[45] An X-ray analysis of **70** showed that the central six-membered ring is still aromatic even though the double bonds in it are localized as indicated in Figure 5.[46]

However, an X-ray analysis of **43a** clearly shows strong localization of the double bonds in the central six-membered ring as indicated in Figure 5.[47] This six-membered ring contains an extremely long $C_{(sp^2)}-C_{(sp^2)}$ bond 1.540(5) Å which is completely identical to a typical $C_{(sp^3)}-C_{(sp^3)}$ bond. Finally, the six-membered ring is no longer aromatic. What kind of structure, therefore, is the most favorable for **43a**? In 1993, Schulman and Disch reported that the C_{2v} form **71a** of benzodicyclobutadiene (**71**) is ca. 10 kcal/mol higher in energy than the C_{2h} forms **71b** or **71c**.[48] However, the bond lengths obtained experimentally for **43a** are closer to a hybrid of the two theoretical C_{2v} isomers **71b** and **71c**. Furthermore, the annulated bonds in **43a** are shorter than the average of the respective bonds in **71b** and **71c**. Finally, it looked like the more stable isomer was not the one that was experimentally found. In order to resolve this dichotomy, ab initio calculations was carried out on **71** at higher theoretical levels.[47]

Table 1 summarizes the geometry of the systems obtained for **71** from these calculations.[47] It was found that there are only two bond-stretch isomers, both possessing C_{2h} symmetry. One is similar to **71a**; the second one, **71d**, does not correspond to either **71b** or **71c** but is similar to the one found in the crystal structure of **43a**. Furthermore, **71d** is theoretically predicted to be 2.4 or 3.7 kcal mol^{-1} (using B3LYP/6131G* or MP2/6–31G*, respectively) more stable than **71a**,[47] although **71a** has been predicted to be more stable than **71b** (or **71c**) by 17.9–20 kcal/mol.[48]

4. Conclusions

Thermal cyclization reactions of diallene derivatives into four-membered ring compounds are shown to proceed efficiently and even stereoselectively in crystals. It is interesting to note that the solid-state reactions which accompany a large molecular motion occur easily. Since the solid-state reaction can be monitored by spectroscopic techniques, the reaction mechanism is analyzed more accurately. The thermal reaction and the photochemical reaction can be carried out in the crystal. Furthermore, since solid-solid, solid-liquid and solid-gas reactions can also be accomplished, most of the usual organic reactions can be carried out in the absence of a solvent. These are simple, economical and pollution-free new synthetic procedures.

By X-ray analysis of the four-membered ring compounds obtained by the solid-state reaction, two new records in chemical bonds were established. The extremely long $C_{(sp^3)}-C_{(sp^3)}$ bond in naphthocyclobutenes (1.720−1.733 Å) would be due to a steric repulsion between the four bulky substituents on the four-membered ring. When more bulky substituents are introduced, much longer C−C bond lengths would be expected. It is interesting to know how long C−C bonds can be without breaking.

For the benzodicyclobutadienes, a benzene ring with an extremely long $C_{(sp^2)}-C_{(sp^2)}$ bond (1.540 Å) was found. This corresponds to a normal saturated C−C bond length. Is the six-membered ring no longer aromatic? Calculations suggest that the ring is still a benzene ring. This is also a new record for a distorted benzene ring. It seems very difficult to destroy the aromatic character of the benzene ring by mechanical processes. It is an interesting challenge to know the limitations of the stable exsistence of benzene nuclei.

The final conclusion is that "the C−C bond and benzene nuclei problems still hold several puzzles and mysteries."

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