Pergamon

Tetrahedron Letters 42 (2001) 7979–7982

TETRAHEDRON
LETTERS

Evidence that naphthocyclobutene, phenanthrodicyclobutene, and anthrodicyclobutene derivatives are not contaminated by their cyclobutene ring-opened isomers†

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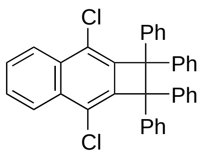
Received 7 June 2001; revised 6 August 2001; accepted 21 August 2001

Abstract—It has not been directly proven that the title cyclobutene derivatives which have an extremely long C*sp*^{3}–C*sp*^{3} bond length of the cyclobutene ring, are not contaminated by their cyclobutene ring-opened isomers. In order to clarify the uncertainties, NO addition experiments were carried out. When the cyclobutene ring is cleaved easily, NO may react with the cyclobutene ring. Although NO did not react with naphthocyclobutene and anthrodicyclobutene derivatives, NO reacted with anthrodicyclobutene derivatives at their central benzene nuclei instead of their cyclobutene rings. These results clearly show that all the cyclobutene derivatives do not exist in an equilibrium with any cyclobutene ring-opened isomer. © 2001 Elsevier Science Ltd. All rights reserved.

We have reported that the C*sp*^{3}–C*sp*^{3} bond length of the cyclobutene ring in naphthocyclobutene (**1**), anthrodicyclobutene (**2**) and phenanthrodicyclobutene (**3**) is extremely long, 1.72–1.73 Å, due to steric repulsion among four phenyl groups on the cyclobutene ring.[1] However, because of the following erroneous history regarding the long bond, chemists are nervous about establishment of the longest bond record. Gomberg's famous discovery[2] of the formation of a triphenylmethyl radical by homolysis of the central long bond in hexaphenylethane proved to be erroneous in 1968,[3] and the central bond length of the hexaphenylethane is also clarified not to be very long. For example, hexakis(2,4-di-*tert*-butylphenyl)-



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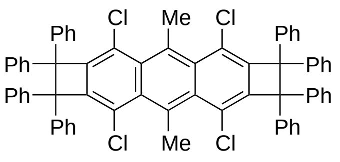

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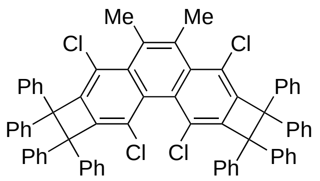

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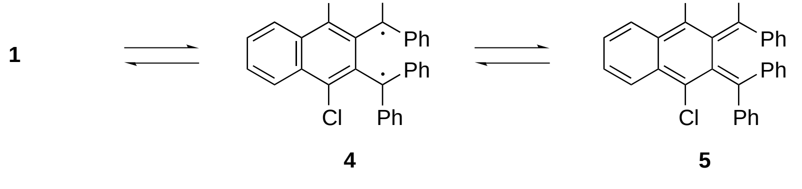

Scheme 1.

Keywords: NO addition to anthracene; anthrodicyclobutene derivatives; the longest C–C bond.

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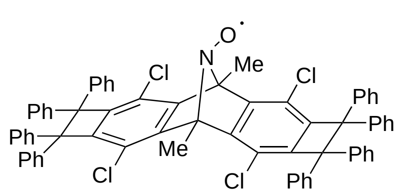
† This paper is dedicated to Professor Masazumi Nakagawa on the occasion of his 85th birthday.

PII: S0040-4039(01)01561-1

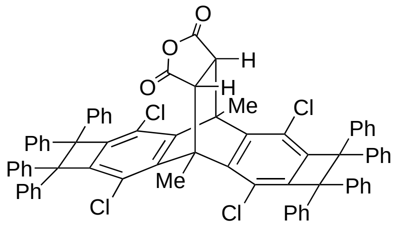
ethane was prepared as the first example of hexaarylethane and its central bond length was found to be 1.67 Å and not to be very long by X-ray analysis in 1986.[4] Cyclobutane (1.77 Å)[5] and bis-norcaradiene (1.83 Å)[6] derivatives prepared from cyclophane and bridged annulene, respectively, by photocyclization have been reported to have a very long C–C bond as indicated. However, the data of both the former[7] and the latter[8] were found to be erroneous, since these samples used for X-ray analysis were contaminated with their starting materials reproduced by reversible ring-opening reactions (Scheme 1).

For compound **1**, for example, contamination with biradical (**4**) and/or quinodimethane (**5**) cannot be ruled out completely, although **1** shows neither a radical signal in the ESR spectrum nor a quinodimethane chromophore in the UV spectrum. In order to prove that **1**–**3** are not contaminated or equilibrated with these ring-opened compounds, their reactions with NO were studied. It has been established that biradical (**9**) and quinodimethane (**10**) generated by photolysis of 2-indanone (**8**) and thermolysis of benzocyclobutene (**11**), respectively, react with NO to give the adduct (**12**) (Scheme 2).[9]

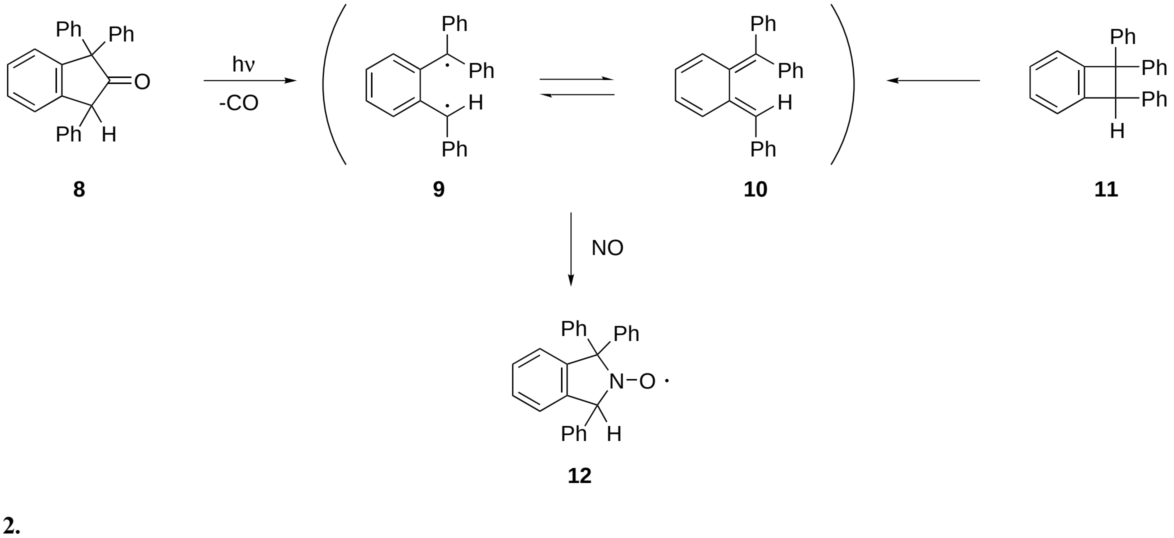
Although neither **1** nor **3** reacted with NO, **2** easily reacted with NO at its central benzene nucleus to give **6**. A solution of **2** in THF saturated with NO was stirred for 30 min at rt. Evaporation of the solvent gave **6**, after recrystallization from THF, as colorless fine crystals, in 84% yield: mp not clear; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.8 (6H, Me), 6.8–7.1 (40H, Ph); UV 247 nm (ε 160,000). The addition reaction can also be carried out in the solid state.[10] When powdered **2** is kept in a flask filled with NO gas for 1 week at rt **6** is produced, after recrystallization from THF, in 51% yield. The structure of **6** was elucidated by comparison of its UV spectrum with that of maleic anhydride adduct (**7**) prepared by the following method. Heating under reflux of a solution of **2** and an equivalent amount of maleic anhydride in toluene for 3 h gave **7**, after recrystallization from acetone, as colorless needles, in 87% yield: mp not clear; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.2 (6H, Me), 3.6 (2H, CH), 6.8–7.0 (40H, Ph); UV 243 nm (ε 460,000). When the same reaction was carried out in the solid state at 100°C for 24 h, **7** was obtained, after recrystallization from acetone, in 65% yield. In both adducts, **6** and **7**, typical UV absorptions for an anthracene chromophore did not appear, but their benzenoid absorptions appeared at 247 and 243 nm, respectively, although yellow colored **2** shows anthracene absorptions at 340–450 nm. By ESR measurement in the solid state, **6** showed the typical spectrum for a nitroxy radical centered at 336 mT, *g* value = 2.006. Although relatively easy Diels–Alder addition reactions of dienophiles to anthracenes have been well established, as we are aware, no easy NO addition reaction to the anthracene ring is known. For example, stirring of a solution of anthracene (**13**) in THF saturated with NO for 24 h at rt gave the adduct **14**, after recrystallization from toluene, as colorless prisms, in only 5% yield: mp 67–70°C; ^{1}H NMR (300



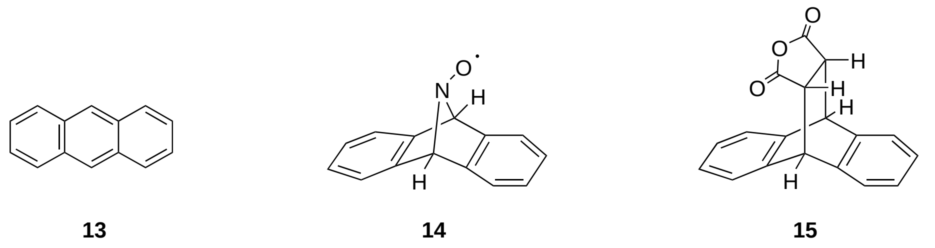
6



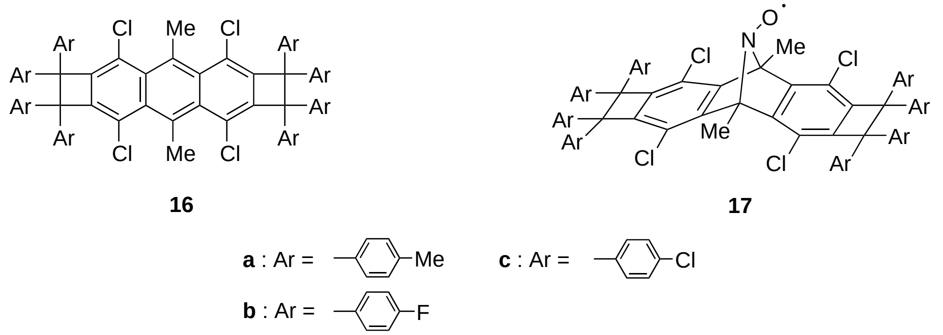
7



Scheme 2.



Scheme 3.



Scheme 4.

MHz, $CDCl_3$) δ 5.0 (2H, CH), 7.2–7.4 (8H, Ph); UV 241 nm (ε 2,700).

What is the main reason for the nonreactivity of the cyclobutene ring in **1**–**3** against NO? The most important reason is attributable to an unstable quinodimethane structure **5** which no longer has aromatic stability. By conversion to the corresponding quinodimethane, **1**–**3** should immediately lose their benzenoid structures. Finally, due to instability of **5**, radical cleavage of **1** to **4** would be unfavorable energetically. Contrarily, the anthracene ring of **2** would become reactive against NO due to a distortion by condensation with two cyclobutene rings, even though steric crowding around the central benzene nucleus is serious. Reversibly, the NO addition releases the steric crowding among the substituents located at the same plane with that of the anthracene ring in **2**. These acceleration effects by the ring strain and the steric factor were also observed for the Diels–Alder reaction. Reaction of **2** with an equimolar amount of maleic anhydride under heating in toluene was completed within 3 h to give **7** in 87% yield, as described above. However, a similar reaction of **13** with six molar amounts of maleic anhydride under the same conditions was completed after 24 h to give the addition product (**15**) in 81% yield (Scheme 3).

In order to confirm that the NO addition to the central benzene nucleus of **2** is a general reaction for anthorodicyclobutene derivatives, the same NO addition reaction was carried out for three derivatives of **2** (**16a**–**c**). Treatment of **16a**–**c** with NO under the same conditions applied to **2** gave **17a**, after recrystallization from THF, in 73% yield: mp >300°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.20 (s, 24H, Me), 2.81 (s, 6H, Me), 6.76–6.81 (m, 32H, Ph); UV 246 nm (ε 40,000), **17b** in 85% yield: mp >300°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.83 (s, 6H, Me), 6.62–7.26 (m, 32H, Ph); UV 244 nm (ε 20,000), and **17c** in 80% yield: mp >300°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.81 (s, 6H, Me), 6.64–7.26 (m, 32H, Ph); UV 250 nm (ε 71,000), respectively.

These data clearly show that the anthracene moieties of **2** and **16a**–**c** condensed with two cyclobutene rings and substituted fully are very reactive to NO, although the highly strained cyclobutene rings are not (Scheme 4).

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture, Japan.

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