

# THERMAL [2 + 2] CYCLOADDITION OF (Z)-[6]PARACYCLOPH-3-ENE WITH TETRACYANOETHYLENE

YOSHITO TOBE\*

*Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560, Japan*

AND

TADAHIRO SORORI, KAZUYA KOBIRO,† KIYOMI KAKIUCHI AND YOSHINOBU ODAIRA

*Department of Applied Fine Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan*

Reaction of (Z)-[6]paracycloph-3-ene (**2**) with tetracyanoethylene (TCNE) gave a [2 + 2] cycloadduct (**4**), which represents the first example of thermal [2 + 2] cycloaddition of a benzene derivative under mild conditions. The structure of **4** was confirmed by x-ray crystallographic analysis. Semi-empirical PM3 calculations and the measurement of the He I photoelectron spectrum of **2** indicated that the ionization potential of **2** is considerably lower than that of [6]paracyclophane (**1**), which gave a [4 + 2] cycloadduct (**3**) with TCNE. The unusual pericyclic selectivity and regioselectivity are discussed on the basis of PM3 calculations. The regioselectivity is ascribed to the higher  $\pi$  bond order of the bridgehead aromatic bond of **2**, which is on the same side of the bridge double bond, than that of the bond on the opposite side of the bridge double bond.

## INTRODUCTION

[*n*]Cyclophanes continue to attract much interest from the viewpoint of strain and aromaticity relationships.<sup>1</sup> It has been well documented that they exhibit remarkably enhanced reactivity and sometimes undergo unusual reactions in electrophilic reactions.<sup>1</sup> Thermal [4 + 2] cycloaddition to electron-deficient olefins and acetylenes is one of such reaction studied in detail. [6]Paracyclophane (**1**)<sup>2</sup> and [5]metacyclophane,<sup>3</sup> the smallest representatives in the *para* and *meta* series that are stable at room temperature, and their derivatives undergo [4 + 2] cycloaddition with dienophiles such as tetracyanoethylene (TCNE), dicyanoacetylene (DCNA), and dimethyl acetylenedicarboxylate.<sup>4,5</sup> On the other hand, Boekelheide and co-workers<sup>6</sup> reported that, under extremely forcing conditions, [2<sub>6</sub>](1,2,3,4,5,6)cyclophane ('superphane') and [2<sub>2</sub>](1,4)cyclophane ([2·2]paracyclophane) gave cycloaddition products with DCNA which were presumably derived by initial [2 + 2] cycloaddition. In contrast, we described in a preliminary report that

(Z)-[6]paracycloph-3-ene (**2**)<sup>7</sup> readily underwent [2 + 2] cycloaddition under mild conditions.<sup>8</sup> Moreover, the reaction took place in a regioselective manner, giving the adduct **4** whose cyclobutane ring is located on the same side of the unsaturated bridge. We report here the structural confirmation of **4** by means of x-ray crystallographic analysis and discuss the pericyclic and regiochemical selectivity on the basis of the semi-empirical molecular orbital calculations.

## RESULTS AND DISCUSSION

When [6]paracyclophane (**1**) was mixed with TCNE in dichloromethane at room temperature, a blue colour ( $\lambda_{\max}$  590 nm) due to the charge-transfer complex developed. The colour gradually disappeared in a few hours to give the [4 + 2] cycloadduct **3** as a single product. In contrast, although blue colour could be discerned in the reaction of cyclophene **2** with TCNE, it disappeared immediately (within 1 s). The reaction was completed within 1 min to yield [2 + 2] cycloadduct **4** as a sole product. The structure of **4** was elucidated on the basis of the <sup>1</sup>H and <sup>13</sup>C

\* Author to whom correspondence should be addressed.

† Present address: Niihama National College of Technology, 7-1 Yagumo-cho, Niihama, Ehime 792, Japan.

NMR spectra. The  $^{13}\text{C}$  NMR spectrum indicates the presence of one trisubstituted  $sp^2$  (C-10) and five disubstituted (C-3, C-4, C-9, C-11, C-12)  $sp^2$  carbons and one trisubstituted  $sp^3$  (C-8) and three tetrasubstituted (C-7, C-13, C-14)  $sp^3$  carbons. These data are consistent with either [2+2] cycloadduct **4** or **5**. The structure was first deduced to be **4** from the  $^1\text{H}$  NMR chemical shift.<sup>8</sup> Support for this assignment was obtained from the NOE experiments; on irradiation of the signals of H-8 and H-9, NOE enhancement was observed for the signals of H-4 and H-3, respectively. It should be pointed out that this reaction represents the first example of thermal [2+2] cycloaddition of a benzene derivative under such mild conditions. Moreover, the reaction took place in a regioselective manner, giving **4** whose cyclobutane ring is located on the same side of the unsaturated bridge.

The structure of **4** was further confirmed by x-ray crystallographic analysis. The molecular structure is shown in Figure 1. The non-bonded distances between the bridge and the six-membered ring (C-3—C-9 = 3.10 Å, C-4—C-8 = 3.45 Å) are longer than that of cyclophene **2** (3.03 Å).<sup>7c</sup> The dihedral angle between the planes C-2—C-3—C-4—C-5 and C-8—C-9—C-11—C-12 is 26.50°, which is larger than the corresponding dihedral angle of **2** (17.70°).<sup>7c</sup> These geometrical differences between **2** and **4** are ascribed to the pyramidalization of C-7 due to the rehybridization from  $sp^2$  to  $sp^3$ . Considerably long bond distances are observed around the cyclobutane ring (C-7—C-13 = 1.606 Å, C-8—C-14 = 1.592 Å, C-13—C-14 = 1.596 Å), indicating that strain is concentrated around the cyclobutane ring. The torsion angle of the

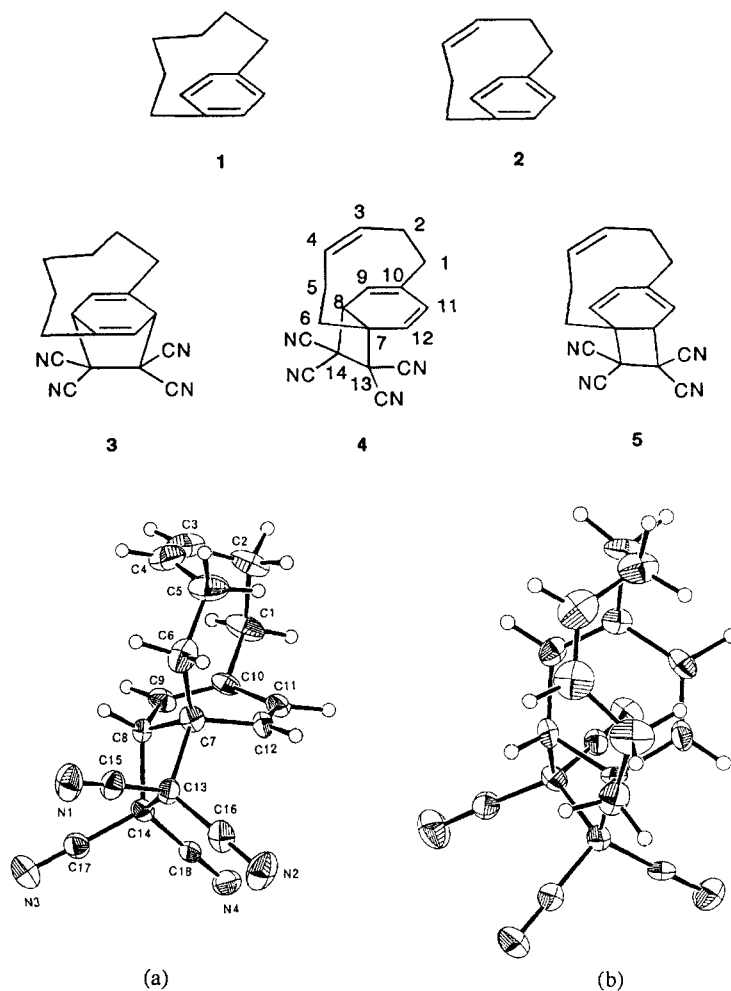


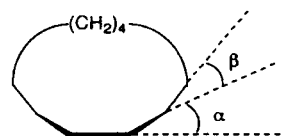
Figure 1. ORTEP drawings of [2+2] cycloadduct **4**. (a) Side view. (b) Top view.

cyclobutane ring, however, is normal; the dihedral angle between the planes C-7—C-8—C-14 and C-7—C-13—C-14 is 29.40°.

The <sup>1</sup>H NMR spectrum of **4** did not show a temperature dependence (–80 to 100 °C), nor was isomerization observed when a solution of **4** was heated in toluene-*d*<sub>6</sub> at 100 °C for 5 h. Prolonged heating or higher temperatures resulted in substantial decomposition of **4**. The experimentally determined barrier for the conformational inversion of bridge in **2** is  $\Delta G^\ddagger = 24.6 \text{ kcal mol}^{-1}$ .<sup>7b,c</sup> Intuitively, it seems unlikely that the barrier of the flipping of **4** is larger than that of **2**, because one of the bridgehead *sp*<sup>2</sup> carbons of **2** rehybridized to an *sp*<sup>3</sup> centre. Although we do not fully understand the discrepancy, one possibility lies in the difference is the isomerization mechanism; cyclophane **2** is capable of isomerizing through C—C bond cleavage and subsequent recombination of the benzyl/allyl diradical intermediate in analogy with the isomerization of [2.2]paracyclophane system,<sup>9</sup> while such isomerization mechanism of **4** is less likely. These results indicate that the barrier for the conformational change (*syn-anti* isomerization) in this system is high and, therefore, the predominant formation of **4** is a result of kinetic control. Indeed, the heats of formation estimated by MM2 calculations for the model hydrocarbons **6** [62.8 kcal mol<sup>-1</sup> (1 kcal = 4.184 kJ)] and **7** (62.6 kcal mol<sup>-1</sup>), which correspond to the respective [2 + 2] adducts **4** and **5**, are almost identical. [4 + 2] Cycloaddition, if it took place, should be thermodynamically favoured since the calculated heat of formation of the [4 + 2]-type hydrocarbon **8** (51.2 kcal mol<sup>-1</sup>) is much less than those of **6** and **7**.

In order to obtain insight into the unusual reactivity of **2**, i.e. the mode of cycloaddition ([2 + 2]) and regioselectivity (*syn* to the bridge), semi-empirical molecular orbital calculations (PM3)<sup>10</sup> were undertaken. The geometries and energies of **2** and those of **1** previously reported<sup>4b</sup> are given in Table 1. As can be seen, the calculated deformation angles ( $\alpha$  and  $\beta$ ) of **2** are larger than those of **1** in accord with the experimental results obtained from the x-ray analyses of their derivatives.<sup>1c</sup> The calculated ionization potential of **2** is lower than that of **1** by 0.12 eV, probably owing to the larger distortion in the aromatic ring of **2**. There seems to be no significant interaction between the aromatic ring and the bridge double bond. To confirm these

Table 1. PM3-calculated geometries, heats of formation and orbital energies and observed ionization potentials of cyclophanes **1** and **2**



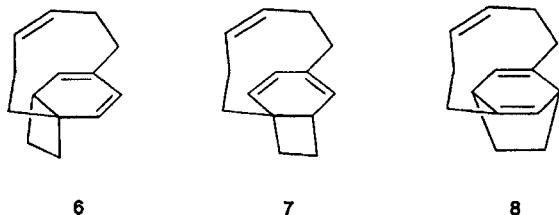
Parameter	<b>1</b>	<b>2</b>
bending angle $\alpha$ , (°)	23.2 <sup>a</sup>	25.4
bending angle $\beta$ (°)	16.8 <sup>a</sup>	19.3
$\Delta H_f^\circ$ (kcal mol <sup>-1</sup> )	30.9 <sup>a</sup>	60.6
Orbital energies (eV):		
$\epsilon_1$	8.77 <sup>a</sup>	8.65
$\epsilon_2$	9.57 <sup>a</sup>	9.52
$\epsilon_3$	—	9.92
Ionization potentials (eV):		
$I_{v,1}$	8.00 <sup>b</sup>	7.76
$I_{v,2}$	8.80 <sup>b</sup>	8.58
$I_{v,3}$	—	9.32

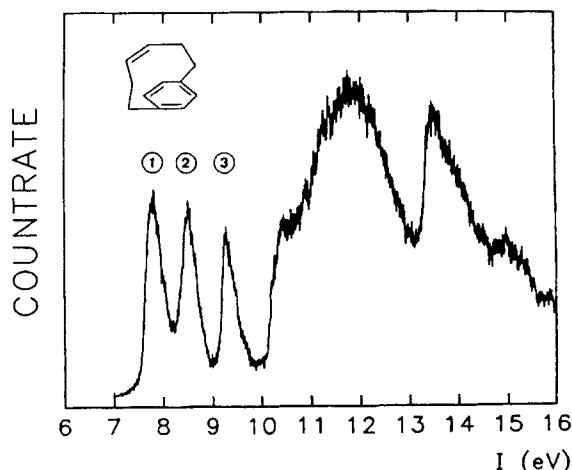
<sup>a</sup> Ref. 4b.

<sup>b</sup> Ref. 12.

predictions, we recorded the He I photoelectron (PE) spectrum of **2**. The PE spectrum of **2** (Figure 2) shows three bands in the low-energy region. To assign these bands to individual transitions, we compared them with related species and made use of Koopman's theorem, which allows one to correlate the measured vertical ionization energies,  $I_{v,j}$ , with the calculated orbital energies. The proper PE data for comparison are those of cyclohexene (9.12 eV)<sup>11</sup> for the olefinic double bond and [6]paracyclophane (**1**) (8.00, 8.80 eV) for the aromatic bonds.<sup>12</sup> This comparison suggests the assignment of the first two bands to ionization from the benzene unit and the third band to the ionization from the double bond. In line with this interpretation are the results of SCF calculations using the PM3 method (Table 1).

It has been well documented that thermal [2 + 2] cycloaddition of olefins with electron-deficient olefins takes place through zwitterion intermediates which are formed by coupling of radical ion pairs generated by initial one-electron transfer.<sup>13</sup> In view of the low ionization potential of **2**, we assume first that the [2 + 2] cycloaddition of **2** with TCNE proceeds through a zwitterion intermediate **9**. If this were the case, it might be possible to explain the regioselectivity of the cycloaddition in terms of the charge distribution in **9**. In this context, we estimated by PM3 calculations the net charge distribution of the model benzenonium ions **10** and **11** which are to be formed by protonation of the bridgehead carbon of **1** and **2**, respectively (Table 2). In the cation **11**, the net charge of C-8 and C-9, which are

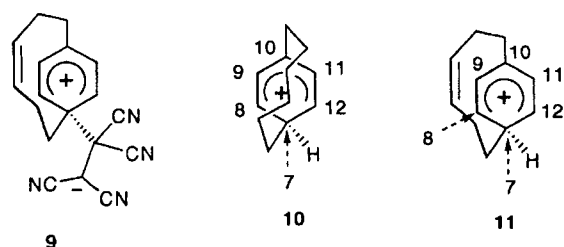
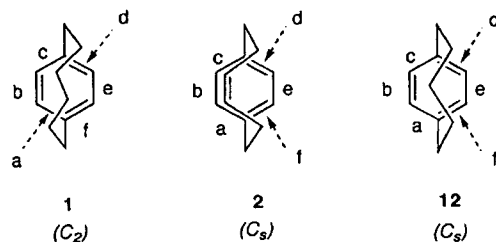


Figure 2. Photoelectron spectrum of **2**.

on the same side of the bridge, is same as those of C-11 and C-12, which are on the opposite side of the bridge. Moreover, the charge distribution of **11** is almost the same as that of **10**, indicating little interaction between the benzenonium ion part and the bridge double bond of **11**. This is probably due to the unfavourable geometry for the two  $\pi$  systems to interact because of the pyramidalization of the bridgehead carbon (C-7), as suggested from the structure of the [2 + 2] cycloadduct **4**. The above results indicate that the regioselectivity should be determined during an earlier stage of the reaction.

Table 3 lists PM3-calculated bond lengths and  $\pi$  bond orders of the aromatic ring of **1**, **2**, and [5]paracyclophane (**12**)<sup>14</sup> The reported geometries of

**1**<sup>15</sup> and **12**<sup>15b,16</sup> calculated by the *ab initio* methods are also listed. Inspection of these data shows that the bond lengths of the [n]cyclophanes are closely related to the symmetry of the molecular framework. Namely, in the case of **2** and **12** having  $C_s$  symmetry, the bond lengths

Table 2 PM3-calculated net charge distributions of benzenonium ions **10** and **11**

Compound	Net charge					
	C-7	C-8	C-9	C-10	C-11	C-12
<b>10</b>	-0.09	0.13	-0.17	0.28	-0.17	0.13
<b>11</b>	-0.08	0.13	-0.17	0.28	-0.17	0.13

Table 3. PM3-calculated bond distances and  $\pi$  bond orders of the aromatic rings of cyclophanes **1**, **2**, and **12**

Compound	Aromatic bond					
	a	b	c	d	e	f
Bond length (Å)						
<b>1</b> <sup>a</sup>	1.401	1.388	1.402	1.401	1.388	1.402
<b>1</b> <sup>b</sup>	1.398	1.392	1.399	1.398	1.392	1.399
<b>2</b>	1.401	1.389	1.401	1.405	1.384	1.405
<b>12</b>	1.404	1.390	1.404	1.409	1.383	1.409
<b>12</b> <sup>c</sup>	1.392	1.401	1.392	1.409	1.384	1.409
$\pi$ Bond order						
<b>1</b> <sup>a</sup>	0.424	0.498	0.422	0.424	0.498	0.422
<b>2</b>	0.430	0.497	0.430	0.403	0.525	0.403
<b>12</b>	0.426	0.505	0.426	0.386	0.552	0.385

<sup>a</sup> Ref. 4b.

<sup>b</sup> *Ab initio* calculations using double-zeta basis set.<sup>15a</sup>

<sup>c</sup> *Ab initio* calculations using double-zeta basis set.<sup>16b</sup>

of the bridgehead aromatic bonds (a and c) on the left side of the molecule are shorter than those of bonds d and f on the right side, although the difference is relatively small. On the other hand, in the case of **1** with  $C_2$  symmetry, the bond lengths of the bridgehead aromatic bonds are almost identical. This trend is also found in the geometries of **1**<sup>15</sup> and **12**<sup>15b,16</sup> obtained by *ab initio* calculations. We noticed that the imbalance between the left and right sides of the molecule is greater for the  $\pi$  bond orders of the bridgehead aromatic bonds of **2** and **12**, i.e. the  $\pi$  bond orders of bonds a and c of **2** are larger than those of bonds d and f. Since the imbalance in the  $\pi$  bond orders of [5]paracyclophane (**12**) is greater than that in **2**, we ascribed it to the symmetry of the molecular framework rather than the interaction between the  $\pi$  orbitals of the aromatic ring and the bridge double bond. Thus the formation of the charge-transfer complex between the electron-deficient olefin (TCNE) with **2** would be kinetically more favoured when TCNE approaches the bridgehead bonds with stronger double bond character. Consequently, we deduce that the regioselectivity observed in the cycloaddition of **2** with TCNE is due to the kinetically favoured geometry of the  $\pi$  complex formed during an early stage of the reaction.

## EXPERIMENTAL

*Reaction of [6]paracyclophane (1) with TCNE.* To a solution of 120 mg (0.94 mmol) of TCNE in 12 ml of dichloromethane was added a solution of **1** (50 mg, 0.31 mmol) in 0.3 ml of the same solvent under nitrogen. The solution turned blue immediately after addition of **1**, and the blue colour then gradually disappeared. The solution was stirred at room temperature for 3.5 h and the solvent was evaporated. Recrystallization of the residue from diethyl ether–dichloromethane gave 54 mg of the adduct **3**. An additional amount of **3** was obtained from the mother liquor by preparative TLC to furnish a total of 71 mg (80%) of **3**, m.p. 196–198 °C (decomposition). <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$  6.25 (d,  $J=6$  Hz, 2H), 4.09 (dd,  $J=6, 2$  Hz, 2H), 2.38 (dt,  $J=11, 2$  Hz, 2H), 2.2–1.6 (m, 6H), 1.2–0.7 (m, 2H), 0.2–0.2 (m, 2H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>),  $\delta$  154.4 (s), 124.9 (d), 113.4 (s), 113.3 (s), 49.5 (d), 44.3 (s), 35.6 (t), 29.1 (t), 25.6 (t); IR (KBr) 2250, 895, 850, 685 cm<sup>-1</sup>; MS,  $m/z$  (relative intensity, %) 288 (M<sup>+</sup>, 10), 160 (26), 104 (100). Analysis calculated for C<sub>18</sub>H<sub>16</sub>N<sub>4</sub>, C 74.97, H 5.59, N 19.43; found, C 74.89, H 5.60, N 19.41%.

*Reaction of [6]paracycloph-3-ene (2) with TCNE.* To a solution of 77.2 mg (0.60 mmol) of TCNE in 8 ml of dichloromethane was added a solution of **2** (30.3 mg, 0.19 mmol) in 0.3 ml of the same solvent under nitrogen. A blue colour appeared, but it

immediately disappeared. The solution was stirred at room temperature for 30 min and the solvent was evaporated. Recrystallization of the residue from diethyl ether–dichloromethane gave 40 mg (73%) of the adduct **4**, m.p. 183–185 °C (decomposition). Attempted chromatography resulted in partial decomposition of **4**. <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$  6.46 (d,  $J=9.9$  Hz, 1H), 5.84 (dd,  $J=9.9, 1.5$  Hz, 1H), 5.66–5.60 (m, 1H), 5.17–5.10 (m, 1H), 4.89 (d,  $J=7.0$  Hz, 1H), 3.73 (dd,  $J=7.3, 1.8$  Hz, 1H), 2.57–2.53 (m, 1H), 2.3–2.0 (m, 6H), 1.86–1.81 (m, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  143.1 (s), 136.7 (d), 133.4 (d), 128.9 (d), 124.9 (d), 112.6 (d), 110.6 (s), 109.5 (s), 109.2 (s), 108.2 (s), 51.9 (s), 48.9 (t), 45.6 (s), 39.2 (s), 37.8 (t), 34.6 (t), 26.5 (t), 23.6 (t); IR (KBr), 2230, 855, 780, 705 cm<sup>-1</sup>; MS,  $m/z$  (relative intensity, %) 286 (M<sup>+</sup>, 13), 158 (22), 104 (100). Analysis calculated for C<sub>18</sub>H<sub>14</sub>N<sub>4</sub>, C 75.50, H 4.93, N 19.57; found, C 75.29, H 4.94, N 19.29%.

*X-ray crystal structure analysis of 4.* Crystal data: C<sub>18</sub>H<sub>14</sub>N<sub>4</sub>,  $M_r=286.34$ , triclinic, space group  $P\bar{1}$ ,  $a=9.722(3)$  Å,  $b=11.691(3)$  Å,  $c=7.445(2)$  Å,  $\alpha=95.14(2)^\circ$ ,  $\beta=109.99(2)^\circ$ ,  $\gamma=85.35(2)^\circ$ ,  $V=790.9(4)$  Å<sup>3</sup>,  $D_c=1.202$  g cm<sup>-3</sup>,  $Z=2$ . Diffraction intensities were measured using a collodion-coated crystal (0.13 × 0.13 × 0.25 mm) on a Rigaku AFC5R diffractometer with graphite monochromated Mo K $\alpha$  radiation. A total of 2967 reflections were collected up to  $2\theta=50.00^\circ$ , among which 2788 were unique. The structure was solved and refined using the program package TEXSAN<sup>17</sup> to the  $R$  index of 0.067 ( $R_w=0.035$ ).

## SUPPLEMENTARY MATERIAL

Tables of bond distances, angles, fractional atomic coordinates, and anisotropic thermal parameters for nonhydrogen atoms for **4**. These material will be available on request to the author.

## ACKNOWLEDGEMENT

The authors are grateful to Professor Rolf Gleiter of the University of Heidelberg for the measurement of the PE spectrum of **2** and for helpful discussions.

## REFERENCES

- For recent reviews, see (a) F. Bickelhaupt and W. H. de Wolf, *Recl. Trav. Chim. Pays-Bas* **107**, 459 (1988); (b) F. Bickelhaupt, *Pure Appl. Chem.* **62**, 373 (1990); (c) W. H. de Wolf and F. Bickelhaupt, in *Advances in Strain in Organic Chemistry*, edited by B. Halton, Vol. 3, p. 185. JAI Press, Greenwich, CT (1993); (d) V. V. Kane, W. H. de Wolf and F. Bickelhaupt, *Tetrahedron* **50**, 4575 (1994); (e) Y. Tobe, *Top. Curr. Chem.* **172**, 1 (1994).

2. (a) V. V. Kane, A. D. Wolf and M. Jones, Jr, *J. Am. Chem. Soc.* **96**, 2643 (1974); (b) S. L. Kammula, L. D. Iroff, M. Jones, Jr, J. W. van Straten, W. H. de Wolf and F. Bickelhaupt, *J. Am. Chem. Soc.* **99**, 5815 (1977); (c) Y. Tobe, K. Ueda, K. Kakiuchi, Y. Odaira, Y. Kai and N. Kasai, *Tetrahedron* **42**, 1851 (1986).
3. (a) J. W. van Straten, W. H. de Wolf and F. Bickelhaupt, *Tetrahedron Lett.* 4667 (1977); (b) L. A. M. Turkenburg, P. M. L. Blok, W. H. de Wolf and F. Bickelhaupt, *Tetrahedron Lett.* **22**, 3317 (1981).
4. For [4 + 2] cycloaddition of **1** and its derivatives, see Ref. 2c and (a) J. Liebe, C. Wolff, C. Krieger, J. Weiss and W. Tochtermann, *Chem. Ber.* **118**, 4144 (1985); (b) Y. Tobe, A. Takemura, M. Jimbo, T. Takahashi, K. Kobiuro and K. Kakiuchi, *J. Am. Chem. Soc.* **114**, 3479 (1992).
5. For [4 + 2] cycloaddition of [5]metacyclophane and its derivatives, see L. W. Jenneskens, H. J. R. de Boer, W. H. de Wolf and F. Bickelhaupt, *J. Am. Chem. Soc.* **112**, 8941 (1990).
6. (a) Y. Sekine and V. Boekelheide, *J. Am. Chem. Soc.* **103**, 1777 (1981); (b) J. E. Garbe and V. Boekelheide, *J. Am. Chem. Soc.* **105**, 7384 (1983).
7. (a) Y. Tobe, K. Ueda, K. Kakiuchi and Y. Odaira, *Angew. Chem., Int. Ed. Engl.* **25**, 369 (1986); (b) Y. Tobe, K. Kaneda, K. Kakiuchi and Y. Odaira, *Chem. Lett.* 1217 (1986); (c) Y. Tobe, K. Ueda, T. Kaneda, K. Kakiuchi, Y. Odaira, Y. Kai and N. Kasai, *J. Am. Chem. Soc.* **109**, 1136 (1987).
8. Y. Tobe, T. Sorori, K. Kobiuro, K. Kakiuchi and Y. Odaira, *Tetrahedron Lett.* **28**, 2861 (1987).
9. H. J. Reich and D. J. Cram, *J. Am. Chem. Soc.* **91**, 3517 (1969).
10. J. J. P. Stewart, *J. Comput. Chem.* **10**, 209 (1989); the calculations were performed using MOPAC Ver. 5.00 (QCPE No. 445); P. J. J. Stewart, *QCPE Bull.* **9**, 10 (1989); T. Hirano, *JCPE Newsl.* **1**, 36 (1989); revised as Ver. 5.01 for OS/2 personal computers: J. Toyoda, *JCPE Newsl.* **2**, 56 (1990).
11. P. Bischof and E. Heilbronner, *Helv. Chim. Acta* **53**, 1677 (1970).
12. H. Schmidt, A. Schweig, W. Thiel, and M. Jones, Jr, *Chem. Ber.* **111**, 1958 (1978).
13. R. Huisgen, *Acc. Chem. Res.* **10**, 117 (1977).
14. L. W. Jenneskens, J. J. de Kanter, P. A. Kraakman, L. A. M. Turkenburg, W. E. Koolhaas, W. H. de Wolf, F. Bickelhaupt, Y. Tobe, K. Kakiuchi and Y. Odaira, *J. Am. Chem. Soc.* **107**, 3716 (1985).
15. (a) T. J. Lee, J. E. Rice, W. D. Allen, R. B. Remington, and H. F. Schaefer, III, *Chem. Phys.* **123**, 1 (1988); (b) M. von Armin and S. D. Peyerimhoff, *Theor. Chim. Acta* **85**, 43 (1993); (c) I. Frank, S. Grimme and S. D. Peyerimhoff, *J. Am. Chem. Soc.* **116**, 5949 (1994).
16. (a) R. B. Remington, T. J. Lee, and H. F. Schaefer, III, *Chem. Phys. Lett.* **124**, 199 (1986); (b) J. E. Rice, T. J. Lee, R. B. Remington, W. D. Allen, D. A. Clabo, Jr, and H. F. Schaefer, III, *J. Am. Chem. Soc.* **109**, 2902 (1987).
17. *TEXRAY Structure Analysis Package*, Molecular Structure Corporation (1985).