

[1.1]Paracyclophane. Photochemical Generation from the Corresponding Bis(Dewar benzene) Derivative and Theoretical Study of Its Structure and Strain Energy

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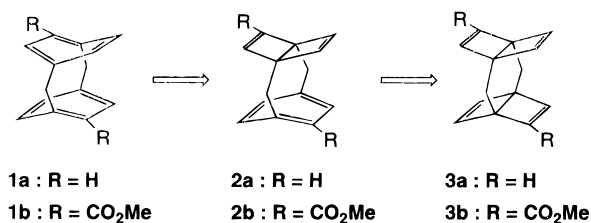
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Abstract: The first generation of [1.1]paracyclophane (**1a**) and its bis(methoxycarbonyl) derivative (**1b**) from the corresponding bis(Dewar benzene) precursors, **3a** and **3b**, has been investigated. Irradiation of **3a** in a glassy mixture of ether–isopentane–ethanol at 77 K leads to the formation of species exhibiting absorption extending to 450 nm, which readily undergoes secondary photolysis to give an isomer showing λ_{max} at 244 nm. On the basis of these UV/vis spectral observations and the accompanying ¹H NMR measurement, the structures of **1a** and the corresponding transannular [4 + 4] adduct (**21a**) are assigned to the initial and the secondary products, respectively. Compound **3b** undergoes similar successive phototransformation into **1b** and **21b**. [1.1]Paracyclophanes, **1a** and **1b**, and their photoisomers, **21a** and **21b**, are sufficiently stable to permit the measurement of ¹H NMR spectra at low temperature, but are consumed fairly rapidly in solution at ambient temperature, defying their isolation. The results of geometrical optimization of **1a** undertaken at the RHF-SCF, MP2, and B3LYP levels employing the 6-31G* basis set are also presented. Calculations indicate that **1a** is a highly strained molecule, but more stable than the related isomers, **3a** and **21a**: the strain energy calculated for **1a** is 128.1, 106.5, and 93.6 kcal/mol at the RHF/6-31G*, B3LYP/6-31G*, and MP2/6-31G* levels, respectively. The closest nonbonding interatomic distance between the aromatic rings in **1a** is in a range of 2.36–2.40 Å, and the degree of bending of the benzene rings is comparable to that in [5]-paracyclophane, much less as compared to that in [4]paracyclophane. Calculations also support strong transannular electronic interactions between the π -bonds of the aromatic moieties of **1a**, which lead to a significantly diminished HOMO-LUMO gap as compared to that in *p*-xylene. The preparation of **3a** and **3b** from diethyl 3,6-dihydroterephthalate in 15 and 11 steps, respectively, is described.

Introduction

Benzene prefers a planar configuration. It is apparently not possible to connect two benzene rings at the 1- and 4-positions with two methylene bridges to produce [1.1]paracyclophane **1** without severely bending bonds, and its construction is seemingly almost prohibitive. Despite its fascinating structure, in which two benzene rings are bent and aligned in parallel in close proximity, and extensive studies on the chemistry of cyclophanes¹ subsequent to the isolation of [2.2]paracyclophane more than 45 years ago,² to our knowledge, no report concerning **1** had been published when we embarked on the preparation of **1** several years ago. Recent successful generation of [4]-paracyclophanes from the corresponding Dewar benzene precursors,^{3,4} however, suggested that **1** and its derivatives might be accessible via valence isomerization of the bis(Dewar benzene) isomers **3** (Scheme 1). The first step of the isomerization (from

Scheme 1



3 to **2**) is nothing else but the production of [4]paracyclophane derivative, if a stepwise process is assumed, and the second step (from **2** to **1**) corresponds to the formation of much less strained, six-carbon-bridged paracyclophane from the corresponding Dewar forms, respectively. Computational analysis on **1–3**, in fact, indicates that the first step will be slightly endothermic whereas the second step will be highly exothermic, suggesting that the latter step should be much easier than the former. Calculations also reveal that the degree of deformation of aromatic ring in **1** will be comparable to that in [5]-paracyclophane,⁵ much less than that in [4]paracyclophane,⁶ implying that **1** may possibly be isolable unless electronic interactions between the aromatic rings held in close proximity significantly destabilize the system.⁷ In a preliminary account of this work⁸ we reported spectroscopic evidence for the generation of the first [1.1]paracyclophane, the bis(methoxy-

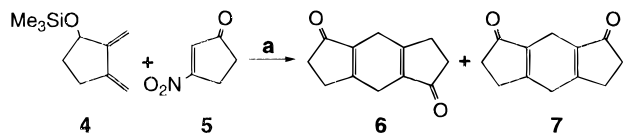
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Scheme 2^a

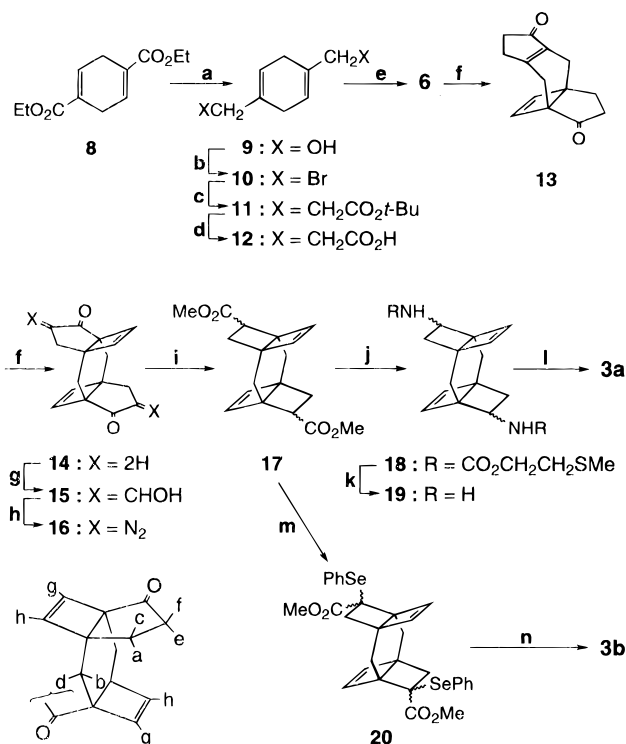
^a Reagents and conditions: (i) 70 °C, 4 h; (ii) DBU; (iii) AcOH-H₂O; (iv) PCC.

carbonyl) derivative. In this paper we present details of the investigation including the theoretical study of 1.

Results and Discussion

Preparation of the Bis(Dewar Benzene) Derivatives (3).

On the basis of our experience on the preparation of Dewar benzene derivatives, tricyclic diketone **6** or **7** was envisioned as the key intermediate for the preparation of **3**. Since those diketones were unknown then, we first investigated their preparation. A convenient synthesis of 4,5,6,7-tetrahydro-1-indanone via the SnCl₄-catalyzed condensation of 1-cyclohexenecarbonyl chloride with trimethylvinylsilane has been reported by Magnus et al.⁹ 3,6-Dihydroterephthaloyl chloride, however, turned out to be rather puzzlingly unreactive under these conditions and provided only an intractable mixture under the more forcing conditions. After several unsuccessful attempts, **6** and **7** were eventually synthesized via the [2 + 4] cycloaddition of 2,3-dimethylenecyclopentyl trimethylsilyl ether (**4**)¹⁰ with 3-nitro-2-cyclopentenone (**5**)¹¹ followed by elimination of nitrous acid, desilylation, and PCC oxidation (Scheme 2). This procedure was rather laborious, and the preparation of **5**, moreover, required the use of concentrated (≥90%) hydrogen peroxide.¹² The diketones thus obtained, however, were found to be relatively stable toward oxidative aromatization and acid- or base-catalyzed isomerization, and their chemical stability prompted us to investigate the preparation of **6** via the acid-promoted intramolecular acylation of unsaturated dicarboxylic acid **12** (Scheme 3).¹³ Compound **12** was prepared from readily available **8**¹⁴ via a sequence in which the latter was successively

Scheme 3^a

^a Reagents and conditions: (a) LAH; (b) PBr₃; (c) AcOt-*t*-Bu/LDA; (d) CF₃CO₂H; (e) (CF₃CO)₂O/BF₃·OEt₂; (f) *hν*/C₂H₂/acetone-CH₂Cl₂; (g) HCO₂Et/NaOEt; (h) TsN₃/Et₃N; (i) *hν*/MeOH; (j) NaOH/H₂O, H₃O⁺, (PhO)₂P(O)N₃/Et₃N, MeSCH₂CH₂OH; (k) Me₂SO₄, NaOH/MeOH-H₂O, H₃O⁺, NaOH; (l) MeI/NaHCO₃, *t*-BuOK/DMF; (m) LDA, PhSeBr; (n) H₂O₂/C₅H₅N.

treated with LAH, PBr₃, *t*-BuOAc/LDA, and CF₃CO₂H. Treatment of the mixed acid anhydride, which was in situ generated from **12** and (CF₃CO)₂O, with BF₃·OEt₂ cleanly provided **6** in 52% yield, in 20% yield overall from **8**.

The photocycloaddition of acetylene to **6** stereoselectively proceeded to furnish *anti*-bis(acetylene) adduct **14** together with several side products. The stereochemical assignment to **14** was based on NOE experiments, in which the methylene bridge protons and the β-endo protons of the cyclopentanone rings were separately irradiated, and was later supported by similar experiments on **3b**. The stereoselective formation of the *anti*-adduct **14** probably resulted from the preferential bending of the central C₆ ring toward the cyclobutene ring in the monoadduct **13** as suggested by force field calculations.¹⁵ Prevailing steric factors would thus guide the entry of the second acetylene anti to the first one. The subsequent transformation of **14** into **3a** and **3b** was carried out in essentially the same manner as reported for the preparation of [4.2.2]propellatetraene.^{4,16} Thus, **14** was diazotized in the usual manner¹⁷ to give **16** which was in turn subjected to photolysis in methanol to furnish diesters **17** as a mixture of three stereoisomers, *syn,syn*-, *syn,anti*-, and *anti,anti*-adducts (with respect to the C₆ ring), in a ratio of 0.9:1.1:1.0. These diesters were separated from each other and their stereochemistries were assigned. In the following reactions, however, they were used as a mixture. The diesters **17** were hydrolyzed to deliver a mixture of carboxylic acids, which were

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(7) [5]Paracyclophane and its derivatives so far prepared are not sufficiently stable to permit their isolation, but persist for a fairly long time in dilute solution in the absence of air at ambient temperature. Van Es, D. S.; de Kanter, F. J. J.; de Wolf, W. H.; Bickelhaupt, F. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2553–2555 and references cited therein.

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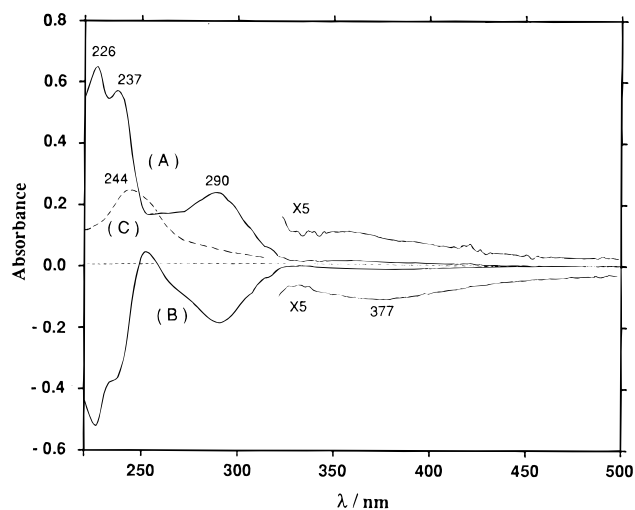


Figure 1. Difference UV/vis spectra (A) between the absorptions before and after the irradiation of **3a** with 254 nm light in EPA at 77 K and (B) between those before and after further irradiation with >335-nm light. Spectrum C was obtained by adding spectrum B to spectrum A.

converted to the isocyanates¹⁸ and then exposed to 2-(methylthio)ethanol to furnish the carbamates **18**. Successive treatment of **18** with dimethyl sulfate and with aqueous NaOH provided carbamate salt, from which a stereoisomeric mixture of amines **19** was liberated through acidification and decarboxylation.¹⁹ The quaternization of **19** with methyl iodide and treatment of the resultant ammonium salt with *t*-BuOK in a DMF/pentane mixture furnished the parent bis(Dewar benzene) **3a** in an overall yield of 15% from **17**. The extremely simple ¹H and ¹³C NMR spectra of **3a**, which consist of only two and three signals, respectively, were fully consistent with its structure, highly symmetrical at least on the NMR time scale.

On the other hand, treatment of **17** with LDA followed by selenenylation with phenylselenenyl bromide afforded a mixture of the phenyl selenides **20**.²⁰ Oxidation of **20** to the selenoxides and the following elimination of benzeneselenenic acid smoothly proceeded to give **3b** as colorless crystals.

Generation of [1.1]Paracyclophanes from the Bis(Dewar benzene) Derivatives in Rigid Glass at Low Temperature. Since the degree of deformation calculated for [1.1]paracyclophane suggested that its thermal stability would be marginal at ambient temperature, the generation of **1** via photolysis of **3** was first investigated under matrix isolation at low temperature. The parent **3a** exhibits only an end absorption extending to ca. 260 nm in its electronic spectrum. Irradiation of a glassy mixture of **3a** in EPA²¹ with a 254-nm light source at 77 K resulted in the development of absorption showing λ_{\max} at 226, 237, and 290 nm, accompanied by a weak, broad band in the region of 330–450 nm (Figure 1A). The generated species was photochemically labile and efficiently consumed when irradiated with filtered light (>335 nm) (Figure 1B), verifying that the weak band in the long-wavelength region was not an artifact. The spectral changes observed upon the secondary photolysis indicated that the initial photoproduct was transformed into the species exhibiting λ_{\max} at 244 nm (Figure 1C). On the basis of these observations and the accompanying ¹H NMR measure-

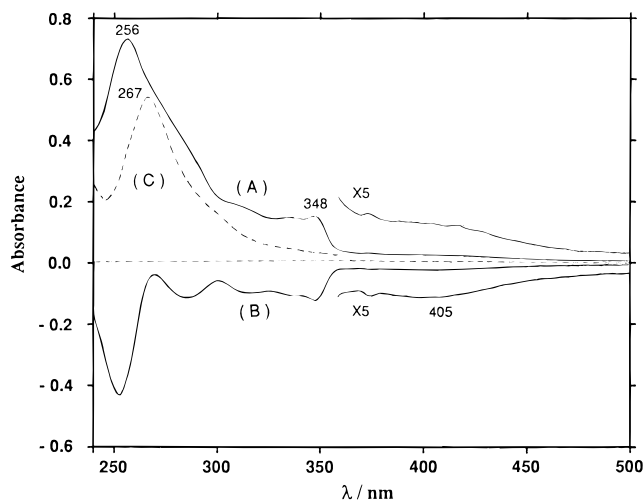
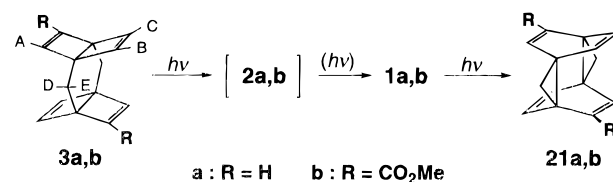


Figure 2. Difference UV/vis spectra (A) between the absorptions before and after the irradiation of **3b** with 254-nm light in EPA at 77 K and (B) between those before and after further irradiation with >390-nm light. Spectrum C was obtained by adding spectrum B to spectrum A.

Scheme 4



ments, the structures of **1a** and **21a** were assigned to the initial and the secondary products, respectively (Scheme 4). It is of interest that **1a** exhibits an absorption band in such a long-wavelength region.

The bis(methoxycarbonyl) derivative **3b** displayed similar photochemical behavior. Thus, irradiation of **3b** in EPA with 254-nm light at 77 K led to the formation of species which exhibited absorption with λ_{\max} at 256 and 348 nm together with a weak, broad band (λ_{\max} at 405 nm) extending to 480 nm (Figure 2A). The newly generated species was rapidly converted to the secondary product showing λ_{\max} at 267 nm upon irradiation with >390-nm light with which only the transient species but not **3b** was electronically excited. The observed spectral changes were attributed to the initial generation of **1b** from **3b** and its secondary transformation into **21b**, on the basis of the accompanying ¹H NMR measurements (vide infra).^{22,23} The UV/vis absorption spectra of **1a** and **1b** remained unchanged for a few hours at -20 °C, indicating that they are sufficiently stable to permit ¹H NMR measurement, but had almost completely decayed after 4 h at room temperature, defying their isolation at ambient temperature.

Measurement of ¹H NMR Spectra of 1a and 1b. The ¹H NMR spectrum of **3b** consists of two singlets due to H_A and the methoxy protons and two pairs of AX doublets due to vicinal H_B/H_C and geminal H_D/H_E. Thus, **3b** is C_i symmetric at least on the ¹H NMR time scale.²⁴ Calculations suggest that the same symmetry is also held in **1b** and **21b**. Irradiation of **3b** with a 254 nm light source in THF-*d*₈ at -70 °C led to the formation

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(20) Reich, H. J.; Wollowitz, S. *Org. React.* **1993**, *44*, 1–216.

(21) A 5:5:2 mixture of diethyl ether, isopentane, and ethanol.

(22) The UV/vis absorptions initially developed upon the irradiation of **3a** and **3b** markedly differ in shape from those of [4]paracyclophane and its methoxycarbonyl derivative, respectively.⁴ Thus, the possibility that the observed spectra were due to **2a** and **2b**, [4]paracyclophane derivatives, is ruled out.

(23) To our knowledge, the photochemical transformation of **1a,b** into **21a,b** represents the first direct formation of benzene *p,p*-dimer.

Table 1. ^1H NMR Parameters for **1b**, **3b**, and **21b**^a

species	H_A (d)	J_{AB} (Hz)	H_B/H_C (d)	J_{BC} (Hz)	H_D/H_E (d)	J_{DE} (Hz)
1b	7.60	2.5	6.95, 7.14	8.8	4.44 ^b	11.7
3b	7.19	<1	6.45, 6.56	2.4	2.38, 2.50	14.6
21b	7.12	<1	6.03, 6.13	6.4	1.95, 2.45	6.6

^a In THF-*d*₈ at -60°C . The signals of OCH₃ were observed at δ 3.94, 3.65, and 3.61 for **1b**, **3b**, and **21b**, respectively. ^b The signal of the other proton could not be identified, probably due to its overlap with one of the much stronger signals due to the methoxy group of **3b** at δ 3.65, the solvent at δ 3.58, and water at δ 3.30.

of two species in ca. 3% and 6% yields at the expense of 10% of **3b**. Both the newly observed two sets of signals are simple, as listed in Table 1, and their characteristics unambiguously indicated that both the generated species also retained the *C*_i symmetry.²⁵ Increase in the vicinal coupling between the olefinic protons H_B and H_C from a small 2.4 Hz, characteristic of cyclobutene,^{26a} to 8.8 Hz in the minor product and 6.4 Hz in the other, moreover, suggested the cleavage of the central bonds of both the Dewar benzene moieties in both products. None of the less symmetrical products resulting from the rearrangement of only one of the Dewar benzenes, e.g., **2b**, was detected by the ^1H NMR. When the resultant NMR sample was irradiated with $>390\text{-nm}$ light, the minor product was quantitatively converted to the major product in close correspondence with the changes in UV/vis absorption, implying that the former is responsible for the absorption extending to 480 nm and the latter for the one showing λ_{max} at 267 nm.

The observed UV/vis spectral changes and the details of ^1H NMR spectra are reasonably accommodated by postulating the initial rearrangement of **3b** into **1b**, which was in turn transformed into **21b** via the transannular [4 + 4] photocycloaddition. The downfield shifts of all the signals due to H_A–H_E, coupled with the appearance of substantial coupling between H_A and H_B, upon the initial isomerization strongly suggest the aromatization of the Dewar benzenes. The subsequent upfield shifts of the methylene proton signals and the decrease in their mutual coupling from the normal 11.7 Hz to 6.6 Hz, typical of cyclopropyl derivatives,^{26b} upon secondary photolysis are also consistent with the proposed transformation. The assignment of the electronic absorption extending to 480 nm to **1b**, which possesses strongly interacting bent benzene chromophores, seems reasonable, and the band at 267 nm is also compatible with that in **21b**.²⁷ Thus, we concluded that **1b** was successfully generated photochemically from **3b**, but prone to undergo the secondary photolysis to give **21b**.

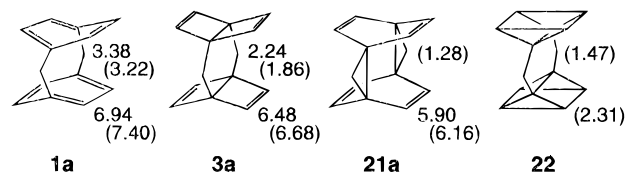
Similar successive transformation was observed for **3a**. Thus, irradiation of **3a** with a 254 nm light source in THF-*d*₈ at -80°C led to the development of three singlets at δ 3.38, 5.90, and 6.94 at the expense of two singlet signals at δ 2.24 and 6.48 due to **3a**. When the resultant mixture was irradiated with $>335\text{-nm}$ light by which **3a** was not affected, the singlet signal at δ 5.90 was enhanced whereas those at δ 3.38 and 6.94 decayed. The former was accordingly assigned to **21a** and the

(24) According to calculations (MNDO and RHF/6-31G*), the central six-membered ring of **3a** is significantly bent in a boat form. Interconversion between the bent conformers would be facile on the NMR time scale at room temperature. By contrast, the optimized structures of **1a** and **21a** are *D*_{2h} symmetric (vide infra).

(25) The ^1H NMR spectra recorded in this experiment were shown in a preliminary account of this work.⁸

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(27) Methyl tetracyclo[4.2.2.2^{2,5}.0^{1,6}]dodeca-3,7,9,11-tetraene-3-carboxylate, which possesses a π -bond system similar to that of **21b**, exhibits λ_{max} at 274 nm.¹⁶

**Figure 3.** Experimental and calculated (in parentheses) ^1H NMR chemical shifts for **1a**, **3a**, **21a**, and **22**.

latter to **1a**. The observed spectra were, however, extremely simple and of low relative intensities,²⁸ and could accidentally be due to unknown products. Therefore, recourse to theoretical calculations was made to confirm the structural assignments. Proton chemical shifts were calculated for **1a**, **3a**, **21a**, and **22** by GIAO²⁹/6-31G* with the RHF/6-31G* geometries by using the Gaussian 94 program package.³⁰ The experimental and computed proton chemical shifts summarized in Figure 3 are in reasonable agreement with each other, supporting the above assignments.³¹ Bis(prismane) **22** of the same symmetry is apparently incompatible with either of the observed spectra. The formation of the less symmetrical **2a** was not detected again. A signal for the methylene bridge protons of **21a** was not identified, probably owing to overlap with the much stronger signal due to the residual protons in the deuterated THF at δ 1.75.

Computational Analysis. The structure of **1a**, its thermodynamic stability relative to related compounds, and the strain energy are of special interest. To gain insights into these points, theoretical analyses were carried out by ab initio and DFT quantum mechanical methods.

(1) **Geometry.** The geometrical optimizations of **1a** and **21a** were undertaken at the Hartree–Fock (RHF-SCF), second-order perturbation (MP2) and density functional B3LYP levels employing the 6-31G* basis set implemented in the Gaussian 94 program package.³⁰ The structures of the related compounds, **2a** and **3a**, were also optimized at the RHF/6-31G* level and with semiempirical MNDO Hamiltonian in the MOPAC 5.0 program.³² An initial exploration of the potential energy surface of **1a** with the 3-21G basis set furnished a single energy minimum corresponding to the *D*_{2h} symmetric **1a**. The optimizations with the 6-31G* basis set were accordingly performed within the constraint of *D*_{2h} symmetry. The optimized geometrical parameters for **1a** are summarized in Tables 2 and 3.

(28) The sample contained **1a**, **21a**, and **3a** in a ratio of ca. 3:2:300 after the initial irradiation with 254-nm light. Extended irradiation did not bring about an appreciable increase in the proportion of (**1a** + **21a**):**3a** and only induced the decomposition of the products and **3a**.

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(31) It is of interest to compare the ^1H NMR spectra of **1a,b** with those of the corresponding [2.2]paracyclophane homologues. The aromatic ring protons of [2.2]paracyclophane resonate at δ 6.47. The protons of [2.2]-paracyclophanedicarboxylic ester corresponding to the H_{A–C} of **1b** resonate at δ 7.17 (d, $J = 1.8$ Hz), 6.68 (dd, $J = 7.7$ and 1.8 Hz), and 6.51 (d, $J = 7.7$ Hz), respectively. Hopf, H.; Lenich, F. T. *Chem. Ber.* **1974**, *107*, 1891–1902.

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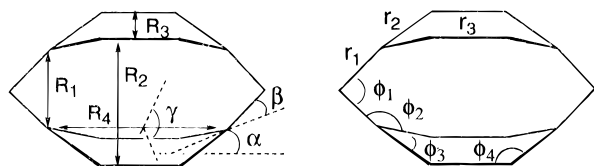


Figure 4. Definition of the deformation angles α – γ , the bond angles ϕ_1 – ϕ_4 , the interatomic distances R_1 – R_4 , and the bond lengths r_1 – r_3 .

Table 2. Calculated Distortion Angles and Nonbonding Interatomic Distances for [1.1]Paracyclophane (**1a**) and the Related Compounds

method	α	β	$(\alpha + \beta)$	γ	R_1	R_2	R_3	R_4
[1.1]Paracyclophane (1a)								
RHF/6-31G*	23.7	26.3	50.0	28.6	2.383	2.982	2.351	2.761
B3LYP/6-31G*	23.3	27.0	50.3	28.3	2.396	2.995	2.371	2.787
MP2/6-31G*	22.5	27.4	49.9	27.2	2.363	2.938	2.378	2.792
[2.2]Paracyclophane ^a								
exptl	12.6	11.2	23.8		2.778	3.093		
[4]Paracyclophane ^b								
DZP ^c	29.7	38.2	67.9	34.1			2.374	2.657
[5]Paracyclophane ^b								
RHF/6-31G	23.5	28.7	52.2	27.2			2.401	2.773

^a From ref 33. ^b From refs 5f and 6a. ^c Double- ζ plus polarization basis set.

Table 3. Calculated Bond Angles and Bond Lengths for [1.1]Paracyclophane (**1a**)

method	r_1	r_2	r_3	ϕ_1	ϕ_2	ϕ_3	ϕ_4
RHF/6-31G*	1.557	1.393	1.390	99.8	118.3	115.1	119.5
B3LYP/6-31G*	1.558	1.406	1.400	100.5	118.6	115.0	118.6
MP2/6-31G*	1.545	1.407	1.401	99.8	118.3	115.3	119.6

For comparison, the data for [2.2]- and [n]paracyclophanes ($n = 4, 5$) from the literature are also listed in Table 2.

The differences between the optimized geometries of **1a** are generally small, $\Delta(\text{bond length}) \leq 0.014 \text{ \AA}$ and $\Delta(\text{bond angle}) \leq 0.7^\circ$. The extent of bond alteration in the aromatic rings is less than 0.006 \AA , small for the significant deformation of the rings, indicating the retention of cyclic delocalization of electrons in the bent benzene rings.³⁴ The transannular distance R_1 is in a range of 2.36–2.40 \AA , shorter by 1.0 \AA than the interlayer distance in graphite (3.35 \AA), suggesting strong electronic interactions between the π bonds of the opposing aromatic rings. The calculated R_2 is also significantly less than 3.35 \AA . Those nonbonding interatomic distances in the MP2/6-31G* structure are somewhat smaller compared to those in the RHF/6-31G* and B3LYP/6-31G* structures.

The bending angle α at the MP2/6-31G* level is slightly smaller, so that the aromatic rings are slightly more flat ($\Delta\gamma \leq 1.4^\circ$) than those at the RHF/6-31G* and B3LYP/6-31G* levels. The total deformation angles ($\alpha + \beta$), however, agree within 0.4° ($50.1 \pm 0.2^\circ$). The angle ($\alpha + \beta$) in **1a** is much smaller than that calculated for [4]paracyclophane,⁶ even slightly smaller than that for [5]paracyclophane.⁵ In accord with the calculation results, **1a** is much superior to the former and is comparable to the latter in kinetic stability. Thus, it appears that the reactivity of **1a** is primarily determined by the extent of bending of the aromatic rings and **1a** is neither particularly stabilized nor destabilized by the close stacking of the benzene rings.

(34) According to recent theoretical calculations, the degree of bond alteration in [4]paracyclophane, the benzene ring of which is more severely bent than that of **1a**, is still small.⁶ The insignificant bond alteration in **1a**, therefore, is not surprising. We recently observed that significant diatropicity is retained in a [4]paracyclophane derivative, suggesting the sustenance of substantial aromatic ring current in its benzene ring. Okuyama, M.; Tsuji, T. *Angew. Chem., Int. Ed.* **1997**, *36*, 1085–1087.

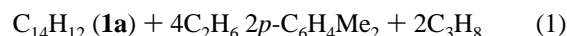
Table 4. Calculated Energies of **2a**, **3a**, and **21a** Relative to **1a** (kcal/mol)

method	1a	2a	3a	21a
MNDO	0 ^a	53.7	45.1	13.7
RHF/6-31G*	0 ^b		51.5	8.7
MP2/6-31G*/RHF/6-31G*	0 ^c			20.0
B3LYP/6-31G*	0 ^d			26.2

^a Heat of formation: $\Delta H_f = 183.5 \text{ kcal/mol}$. ^b Total electronic energy: -536.962707 (b), -538.791204 (c), and -540.563026 au (d).

(2) **Energy.** In Table 4 are listed calculated energy differences of **1a** and the related compounds. Inspection of the table reveals that **1a** is predicted to be the most stable of the calculated isomers, more stable than **21a**, irrespective of the computation methods and theoretical levels. In the generation of **1a** via the photochemical isomerization of **3a**, the accompanying production of **21a** was unavoidable even at the low conversion of **3a**, since the isomerization of **1a** to **21a** proceeded in preference to that of **3a** to **1a** owing to the preferential absorption of irradiated light by **1a**, coupled with its high photochemical reactivity to afford **21a**. The above calculations suggest that thermolysis may be superior to photolysis for the preparation of **1a** from **3a**, provided that the requisite reaction conditions are sufficiently mild to secure **1a** from potential secondary reactions. As mentioned in the introduction, the calculations also indicate that the isomerization of **3a** to **2a** is endothermic whereas that of **2a** to **1a** is strongly exothermic, suggesting that the latter process is significantly more facile than the former. Accordingly, it is not unreasonable that **2a** and **2b** were not detected in the photolysates of **3a** and **3b**, respectively, though a stepwise mechanism was likely in operation.

Although **1a** is the most stable of the calculated isomers, **1a** is still a highly strained molecule. For the evaluation of strain energy in **1a**, 9,10-dihydroanthracene, which possesses two benzene rings bridged by two methylenes as **1a** and yet is strain-free, serves as an ideal reference compound. The total strain energy of **1a** thus evaluated is 128.1, 93.6, and 106.5 kcal/mol at the RHF/6-31G*, MP2/6-31G*, and B3LYP/6-31G* levels, respectively, and is in good agreement with the values evaluated by using the homodesmic reaction 1, 127.8 kcal/mol at the RHF/6-31G* level and 90.8 kcal/mol at the MP2/6-31G* level.



The close face-to-face arrangement of the two bent aromatic rings in **1a** suggests strong electronic interactions between them. The RHF/6-31G* calculations confirm that the HOMO and LUMO of **1a** are significantly raised and lowered in energy, respectively, as compared to those of *p*-xylene as the result of bending of the benzene rings and of their mutual electronic coupling. In Figure 5 is depicted a qualitative derivation of high energy occupied and low energy unoccupied orbitals of **1a** from those of planar *p*-xylene. The distortion of C_{2v} -*p*-xylene to the geometry present in **1a** leads to the destabilization of $b_2(\pi)$ and the stabilization of $a_1(\pi^*)$ MO while leaving the a_2 and b_1 MOs virtually unperturbed. The through-space and through-bond coupling of the resulting b_2 orbitals in **1a** yields b_{1g} and b_{3u} MOs and that of the a_1 MOs leads to MOs of a_g and a_{2u} symmetries. The a_2 and b_1 MOs mutually interact respectively, predominantly through space, to yield the b_{3g}/b_{1u} and a_u/b_{2g} MOs of **1a**. The decreased HOMO-LUMO gap in **1a** (8.83 eV) as compared to that in *p*-xylene (12.33 eV) manifests itself in the UV/vis absorption extending to 450 nm. The physical and chemical consequences of bending of the aromatic rings and of those orbital interactions in **1a** are now under investigation.

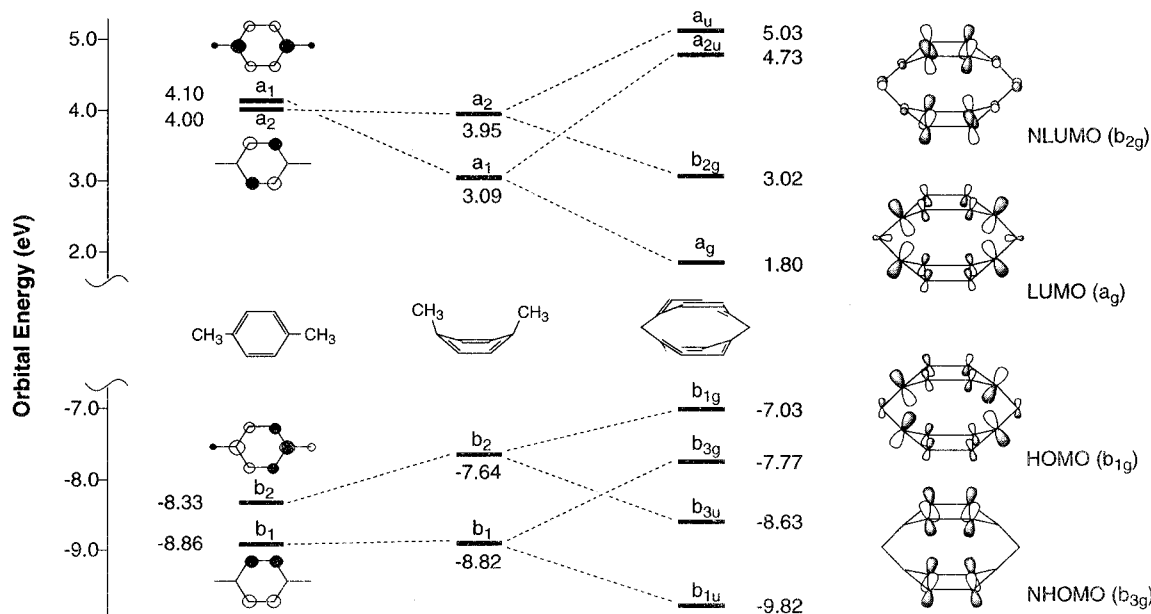


Figure 5. Derivation of the high energy occupied and low energy unoccupied MOs of [1.1]paracyclophane (**1a**) from those of planar C_{2v} -*p*-xylene and schematic representations of the HOMO, NHOMO (N denotes next), LUMO, and NLUMO of **1a** (RHF/6-31G* at the MP2/6-31G*-optimized geometries).

Conclusions

[1.1]Paracyclophane and the bis(methoxycarbonyl) derivative were successfully generated for the first time via the photoisomerization of the corresponding bis(Dewar benzene) precursors. They exhibit UV/vis absorptions extending to unusually long wavelength and undergo unprecedented transannular photocycloaddition between the benzene rings to give the corresponding *p,p*-dimer structures, reflecting the strong electronic interactions between the bent aromatic ring moieties. Theoretical calculations on [1.1]paracyclophane reveal that the extent of distortion of the benzene rings is comparable to that in [5]-paracyclophane and that the shortest transannular interatomic distance is 2.36–2.40 Å, being shorter by 1.0 Å than the interlayer distance in graphite. The calculated strain energy of [1.1]paracyclophane is in a range of 93–128 kcal/mol depending on the level of theory. The [1.1]paracyclophanes prepared in this study are, however, thermally labile and persist only below $-20\text{ }^{\circ}\text{C}$ in solution, necessitating their kinetic stabilization for isolation.

Experimental Section

Halos (Eiko-sha, Japan) 500-W high-pressure and 120-W low-pressure mercury lamps were employed as the light sources of photochemistry. A 500-W high-pressure mercury lamp fitted with a Corning 0-52 glass filter was used as a $>335\text{-nm}$ light source and a 500-W xenon lamp fitted with a Corning 3-73 glass filter as a $>390\text{-nm}$ light source.

Measurement of Electronic Absorption Spectrum of 1a. A solution of **3a** (1 mg, freshly purified by preparative GLC) in 4.9 mL of EPA was placed in a quartz cuvet, degassed by freeze–pump–thaw cycles, and frozen in liquid nitrogen to give a clear, colorless glass. The mixture exhibited only an end absorption extending to 260 nm and an absorbance at 220 nm was 1.2. Irradiation of the glass with a 120-W low-pressure mercury lamp led to development of absorption with λ_{max} at 226, 237, 290, and 377 nm. After 10 min, absorbances at those λ_{max} in the difference spectrum were 0.65, 0.57, 0.24, and 0.02, respectively. When the resulting glass was irradiated with $>335\text{-nm}$ light by which only the newly generated species was excited, the developed absorption was efficiently bleached and the observed spectral changes indicated that the initial product was transformed into a secondary product showing λ_{max} at 244 nm.

The thermal stability of **1a** was examined in a separate experiment. A degassed solution of **3a** in EPA was irradiated with a 254 nm light source at 77 K to generate **1a**, thawed at $-90\text{ }^{\circ}\text{C}$, and refrozen in a liquid N_2 bath. After recording an UV–vis absorption spectrum, the glassy mixture was thawed, kept at $-20\text{ }^{\circ}\text{C}$ for 1 h, and frozen again. The spectrum then recorded indicated that **1a** remained unchanged. After 1 h at $20\text{ }^{\circ}\text{C}$, however, the characteristic bands due to **1a** had largely decayed.

Measurement of the Electronic Absorption Spectrum of 1b. A glassy solution of **3b** (1 mg) in 4.8 mL of EPA in a quartz cuvet at 77 K was prepared as described above for **3a**. The solution exhibited λ_{max} at 235 (absorbance = 3.37) and 259 (2.29) nm and a shoulder at 316 (0.41) nm. Irradiation of the glass with a low-pressure mercury lamp led to development of absorption showing λ_{max} at 256, 348, and 405 nm. After 10 min, absorbances at those λ_{max} in the difference spectrum were 0.73, 0.15, and 0.03, respectively. When the resulting glass was irradiated with $>390\text{-nm}$ light, the developed absorption was almost completely bleached and the observed spectral changes indicated that the initial product was transformed into a secondary photoproduct showing λ_{max} at 267 nm.

The thermal stability of **1b** was examined in a separate experiment. A degassed solution of **1b** was prepared as described above and its decay was monitored spectrometrically. The observed spectral changes indicated that **1b** remained unchanged after 2 h at $-20\text{ }^{\circ}\text{C}$, but had decayed to half the initial concentration after 6 days at the same temperature. After 4 h at $20\text{ }^{\circ}\text{C}$, the absorption due to **1b** had almost completely decayed.

Measurement of the ^1H NMR Spectrum of 1a. In a quartz NMR tube was placed a solution of **3a** (ca. 2 mg) in 0.6 mL of $\text{THF-}d_8$ to which a small amount of tetramethylsilane in CCl_4 was added. The solution was degassed by freeze–pump–thaw cycles and then saturated with argon. The tube was sealed with vaseline and connected to a mechanical stirrer to be rotated during irradiation. The ^1H NMR spectrum (500 MHz) recorded at $-60\text{ }^{\circ}\text{C}$ after irradiating the sample for 4 min with a low-pressure mercury lamp at -85 to $-80\text{ }^{\circ}\text{C}$ indicated the formation of **1a** and **21a** in a ratio of ca. 3:2 in a yield of ca. 2%. Upon further irradiation with a $>335\text{-nm}$ light source, the former was cleanly transformed into the latter as demonstrated in the difference spectrum. When the resulting mixture was left to stand for 1 h at room temperature, **21a** had completely disappeared.

Measurement of the ^1H NMR spectrum of 1b. In a quartz NMR tube was placed a solution of **3b** (5 mg) in 0.6 mL of $\text{THF-}d_8$ to which a small amount of tetramethylsilane in CCl_4 was added. The solution was degassed by freeze–pump–thaw cycles and then saturated with

argon. The tube was sealed with vaseline and connected to a mechanical stirrer to be rotated during irradiation. The ¹H NMR spectrum (500 MHz) recorded at -60 °C after irradiating the solution for 15 min at -70 °C with a low-pressure mercury lamp indicated the formation of **1b** and **21b** in 2-3% and 5-6% yield, respectively, at the expense of ca. 10% of **3b**. Upon further irradiation with a >390 nm light source, the generated **1b** was cleanly transformed into **21b** as demonstrated in the difference spectrum. When the resulting mixture was left to stand for 1 h at room temperature, **21b** had completely disappeared.

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Supporting Information Available: Full experimental details for the preparation of all the compounds reported in the paper (13 pages). See any current masthead page for ordering and Internet access instructions.

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