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Molecular Structures of Diarylcyclobutanes Associated with Reactivities in Ring-Cleavage Reactions: Implications of Conformationally Controlled Through-Bond Coupling

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Molecular structures of diarylcyclobutanes (**1**—**6**) have been determined by single-crystal X-ray analyses. Although the distances and angles of the cyclobutane rings are relatively normal, the torsional angles between the aryl ring and the plane involving the ipso carbon and the aryl-substituted carbons of cyclobutane ring are close to 90° in cases of **1**—**4**, but very small (2.3—11.3 °) in cases of **5** and **6**; conformations of the aryl substituents are highly restricted by the rigid tricyclic structure or by nonbonding interactions between the vicinal substituents in the cis configuration. Restricted conformations are closely related to the different reactivities of the cyclobutane in photochemical, thermal, and radiation-induced ring-splitting reactions. The structure-reactivity relationships are discussed in terms of the conformation-controlled π-σ orbital interactions associated with the capabilities of the π electron systems in through-bond coupling.

The chemistry of cyclobutanes has been of stereochemical significance as a suitable probe for the exploration of both steric and electronic effects on chemical reactivities and as a prototype for theoretical investigations of chemical reaction courses. It can be expected that the chemical behavior of cyclobutanes is remarkably susceptible to a variety of steric and electronic perturbations, since the cyclobutane rings are relatively rigid with small conformational mobilities,[1] and since the molecular-orbital of the ring σ framework shows a small, but significant, π-bonding character.[2] Indeed, we found that aryl-substituted cyclobutanes reveal remarkable structure dependences in photochemical,[3–7] radiation-induced,[8] and thermal[9] ring-splitting reactions as well as in electrochemical oxidation potentials.[3] For instance, the head-to-head transoid cyclobutane dimer of indene (**1**) and related diarylcyclobutanes of "head-to-head" structure are efficiently split into the corresponding olefins by the redox photosensitization that proceeds by way of the π complex with the cation radical of aromatic hydrocarbons (Fig. 1). By contrast, no redox-photosensitized ring splitting occurs at all for the head-to-tail transoid dimer of indene (**2**), other "head-to-tail" diarylcyclobutanes, and monoarylcyclobutanes. Similarly, the head-to-head cisoid dimers of 1,3-dimethylthymine and 1,3-dimethyluracil are efficiently monomerized by redox photosensitization, while the head-to-tail isomers are not at all.[10]

These observations have been interpreted as the consequences of the structure-controlled capabilities of the two π or n electron systems in electronic coupling through the ring σ orbitals, since the "head-to-head" structures are requisite for efficient through-bond coupling. Through-bond coupling has been investigated from theoretical[11] and spectroscopic[12] points of view and has been suggested to play important roles in the photochemical and thermal reactions of some rigid polycyclic compounds with separated π chromophores which are perpendicular to each other.[13] It is, however, predicted that if through-bond coupling is essential in chemistry of diarylcyclobutanes,

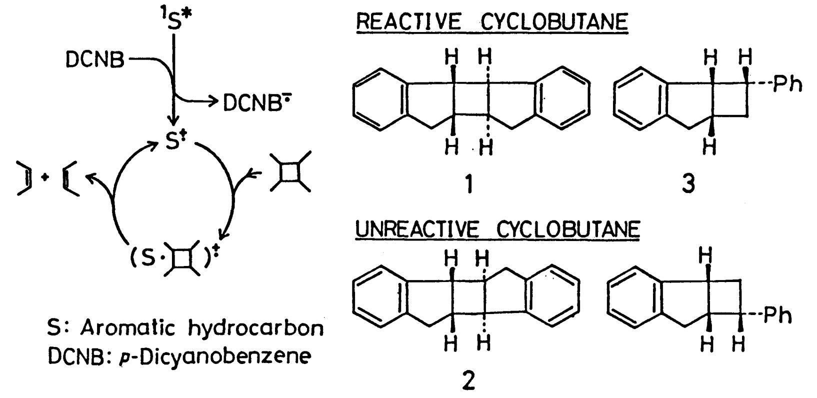
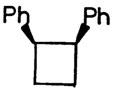


Fig. 1. Redox-photosensitized splitting of the cyclobutane ring; typical "head-to-head" diarylcyclobutanes which are reactive and typical "head-to-tail isomers which are unreactive

conformations of the aryl substituents should control the stereochemical reaction courses. However, little has been known on what relationships exist between the conformational effects on the chemical reactivities and stereochemical requirements for through-bond coupling. Another important expectation is that through-bond coupling would bring about an unusual elongation of a cyclobutane-ring σ bond to activate the "head-to-head" cyclobutanes[14,15] or may stabilize transition states of the ring-splitting reactions by extended electronic conjugation over relevant orbital arrays. From the above-mentioned points of view, we have performed X-ray crystallographic analyses of diarylcyclobutanes **1**—**6** in order to determine the exact molecular structure. In this paper we wish to report on the results and to discuss the implications of molecular structures in the through-bond coupling associated with the reactivities of the cyclobutanes.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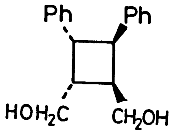
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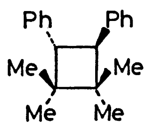
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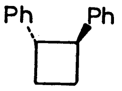
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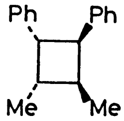
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Experimental

Materials. The preparation of the cyclobutanes was carried out according to reported methods; *cis-transoid-cis*-cyclobuta[1,2-*a*;4,3-*a′*]diindene (**1**),[16] *cis-transoid-cis*-cyclobuta[1,2-*a*;3,4-*a′*]diindene (**2**),[3] *endo*-2-phenyl-2,2a,7,7a-tetrahydro-1*H*-cyclobut[*a*]indene (**3**),[3] *cis*-1,2-diphenylcyclobutane (**4**),[17] *r*-1,*t*-2-bis(hydroxymethyl)-*t*-3, *c*-4-diphenylcyclobutane (**5**),[5] 1,1,2,2-tetramethyl-*trans*-1,2-diphenylcyclobutane (**6**),[18] *trans*-1,2-diphenylcyclobutane (**7**),[17] and *r*-1,*t*-2-dimethyl-*t*-3,*c*-4-diphenylcyclobutane (**8**).[5] Single crystals for X-ray analyses were obtained by recrystallization from methanol for **1**—**5** and from hexane for **6**. On the other hand, all attempts failed in obtaining single crystals of **7** and **8**; these cyclobutanes remained oily at room temperature.

Single-Crystal X-Ray Analysis. Crystal structure analyses were carried out on an Enraf Nonius automated four-circle X-ray diffractometer (CAD 4) using graphite-monochromated Mo *Kα* radiation (λ=0.71073 Å). Intensity data were collected by ω-2θ scan upto 50° for **1**, **4**, and **6**, 60° for **2**, 54° for **3**, and 56° for **5** in 2θ. The crystallographic data are shown in Table 1.

Structure Determination. All of the calculations were carried out on a DEC PDP 11/34 system using a SDP and SDP-Plus programs. The structures were solved by the direct method (MULTAN 82) and refined by a full-matrix least-squares method.

In the last cycle of the refinement with anisotropic temperature factors for nonhydrogen atoms, all of the parameter shifts were less than one-third of the corresponding standard deviations. After the refinement hydrogen atoms were located in positions calculated for a C-H bond length=0.950 Å. Tables of the observed and calculated structure factors, anisotropic temperature factors, and bond distances and angles have been deposited to the Chemical Society of Japan (Document No. 8874).

^{1}H NMR spectra were taken on a JEOL JNM-PS-100 spectrometer for a $CDCl_3$ solution using tetramethylsilane as the internal standard.

Results and Discussion

Molecular Structures. Table 2 lists the final atomic parameters. The crystal packing diagrams and computer-generated molecular structures of **1**—**6** are shown in Figs. 2 and 3, respectively. For the present investigation, the essential structure parameters are the bond distances and angles of the cyclobutane ring,

Table 1. Crystallographic Data and Experimental Conditions

	1	2	3	4	5	6
Formula	$C_{18}H_{16}$	$C_{18}H_{16}$	$C_{17}H_{16}$	$C_{16}H_{16}$	$C_{18}H_{20}O_2$	$C_{20}H_{24}$
Formula wt	232.33	232.33	220.32	208.31	268.36	264.42
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*Pbca*	$P2_1$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/n$
a/Å	12.510(2)	7.162(2)	13.290(2)	7.013(12)	6.392(1)	10.014(3)
b/Å	13.805(9)	6.320(3)	5.842(11)	12.193(3)	15.783(3)	16.749(2)
c/Å	14.897(4)	13.647(2)	17.003(2)	14.302(6)	14.721(3)	19.671(4)
β/deg	—	97.60(8)	109.44(1)	88.56(9)	89.13(5)	76.68(6)
V/Å^3	2572.7	612.4	1244.8	1222.6	1484.8	3210.5
D_{obsd}/g cm^{-3}	1.200	1.260	1.176	1.132	1.200	1.094
D_{calcd}/g cm^{-3}	1.18	1.250	1.16	1.13	1.18	1.10
Z	8	2	4	4	4	8
R_w	0.077	0.071	0.120	0.106	0.096	0.083
R	0.072	0.060	0.085	0.105	0.080	0.070
No. refl. obsd.	8783	1624	2495	1416	1529	3981
No. unobsdly weak refl.	5404	1950	1691	699	970	5162

Table 2. Final Atomic Coordinates with Their Estimated Standard Deviations and Temperature Factors

Atom	x	y	z	B_{eq}/Å^{2} a)
cis-transoid-cis-Cyclobuta[1,2-*a*; 4,3-*a′*]diindene (**1**)				
C1	0.3337(9)	0.5671(8)	0.0220(8)	4.3(3)
C2	0.3367(10)	0.6686(8)	−0.0226(8)	4.3(3)
C3	0.2129(9)	0.6810(8)	−0.0043(7)	3.8(3)
C4	0.2080(9)	0.5697(7)	0.0191(7)	3.9(3)
C5	0.2604(11)	0.3915(9)	−0.1618(8)	5.4(3)
C6	0.1603(13)	0.3826(10)	−0.2007(8)	7.4(4)
C7	0.0701(11)	0.4342(9)	−0.1724(8)	6.1(4)
C8	0.0785(10)	0.4963(9)	−0.1012(8)	5.0(3)
C9	0.1780(9)	0.5071(8)	−0.0599(7)	4.1(3)
C10	0.2693(12)	0.4565(8)	−0.0891(7)	5.2(3)
C11	0.3245(10)	0.8492(9)	0.1664(8)	5.0(3)
C12	0.2324(13)	0.8683(9)	0.2154(8)	7.0(4)
C13	0.1303(11)	0.8319(9)	0.1980(8)	5.9(4)
C14	0.1215(9)	0.7685(8)	0.1272(8)	4.8(3)
C15	0.2098(9)	0.7475(9)	0.0759(7)	4.1(3)
C16	0.3123(8)	0.7829(8)	0.0950(8)	3.9(3)
C17	0.3691(10)	0.4809(9)	−0.0382(9)	5.6(3)
C18	0.3947(8)	0.7480(10)	0.0311(8)	4.9(3)
cis-transoid-cis-Cyclobuta[1,2-*a*; 3,4-*a′*]diindene (**2**)				
C1	0.1569(8)	0.6744(9)	0.7969(4)	3.2(1)
C2	0.3556(6)	0.7162(9)	0.7642(4)	2.54(9)
C3	0.3387(7)	0.5114(8)	0.7004(4)	2.8(1)
C4	0.1421(9)	0.4701(7)	0.7303(5)	3.5(1)
C5	−0.2452(9)	0.774(1)	0.6024(5)	4.3(1)
C6	−0.3105(9)	0.639(1)	0.5199(4)	4.6(1)
C7	−0.2355(9)	0.450(1)	0.5081(5)	4.3(1)
C8	−0.0910(8)	0.384(1)	0.5739(5)	4.0(1)
C9	−0.0127(7)	0.5035(8)	0.6531(4)	3.0(1)
C10	−0.1018(7)	0.7081(8)	0.6640(4)	2.60(9)
C11	0.5860(8)	0.8000(9)	0.9244(4)	3.2(1)
C12	0.7403(8)	0.726(1)	0.9905(4)	3.9(1)
C13	0.8230(7)	0.528(1)	0.9791(5)	3.9(1)
C14	0.7531(7)	0.4062(9)	0.9026(4)	3.3(1)
C15	0.5954(8)	0.4746(9)	0.8310(5)	3.6(1)
C16	0.5244(7)	0.6668(9)	0.8448(4)	3.0(1)
C17	−0.0018(8)	0.8199(9)	0.7556(4)	3.3(1)
C18	0.5054(8)	0.363(1)	0.7432(5)	4.0(1)
endo-2-Phenyl-2,2a,7,7a-tetrahydro-1*H*-cyclobut[*a*]indene (**3**)				
C1	0.8891(4)	−0.0304(8)	0.8705(3)	3.7(1)
C2	0.9543(4)	−0.2607(9)	0.8917(4)	4.6(1)
C3	0.8659(5)	−0.3499(9)	0.9266(3)	5.0(1)
C4	0.8244(4)	−0.1026(9)	0.9290(3)	3.9(1)
C5	0.7096(4)	−0.0550(8)	0.9052(3)	3.5(1)
C6	0.6758(5)	0.1375(9)	0.9371(3)	4.8(1)
C7	0.5667(5)	0.187(1)	0.9162(4)	6.3(2)
C8	0.4892(5)	0.048(1)	0.8623(4)	5.8(1)
C9	0.5246(5)	−0.142(1)	0.8302(4)	5.9(2)
C10	0.6326(4)	−0.1929(9)	0.8504(3)	4.7(1)
C11	0.8319(3)	−0.0483(7)	0.7785(3)	3.22(9)
C12	0.7560(4)	0.0997(8)	0.7280(3)	3.7(1)
C13	0.7124(4)	0.055(1)	0.6432(3)	4.8(1)
C14	0.7440(5)	−0.136(1)	0.6086(3)	5.4(1)
C15	0.8211(4)	−0.2864(9)	0.6595(3)	5.1(1)
C16	0.8655(4)	−0.2405(8)	0.7446(3)	3.9(1)
C17	0.9533(4)	−0.3644(9)	0.8101(4)	5.2(1)
cis-1,2-Diphenylcyclobutane (**4**)				
C1	0.3663(8)	−0.0064(5)	0.1706(4)	5.2(1)
C2	0.2070(9)	−0.0943(5)	0.1806(4)	5.2(1)
C3	0.079(1)	−0.0227(6)	0.1228(5)	6.6(2)
C4	0.256(1)	0.0369(6)	0.0870(5)	7.1(2)
C5	0.3815(8)	0.0697(5)	0.2524(4)	4.8(1)
C6	0.5002(9)	0.0404(5)	0.3262(4)	5.5(1)
C7	0.517(1)	0.1051(6)	0.4019(5)	6.7(2)
C8	0.418(1)	0.2021(6)	0.4088(5)	7.1(2)
C9	0.3000(9)	0.2297(5)	0.3397(5)	6.6(2)
C10	0.2807(9)	0.1655(5)	0.2610(4)	5.4(1)
C11	0.1517(8)	−0.1338(5)	0.2781(4)	4.8(1)
C12	0.2354(9)	−0.2248(5)	0.3135(4)	5.4(1)
C13	0.188(1)	−0.2599(6)	0.4025(6)	7.6(2)
C14	0.058(1)	−0.2063(6)	0.4587(5)	6.7(2)
C15	−0.025(1)	−0.1172(6)	0.4202(5)	7.0(2)
C16	0.0145(9)	−0.0788(5)	0.3341(4)	5.7(2)
r-1,*t*-2-Bis(hydroxymethyl)-*t*-3,*c*-4-diphenylcyclobutane (**5**)				
C1	0.737(1)	0.5445(3)	0.2372(3)	2.9(2)
C2	0.788(1)	0.4492(3)	0.2344(3)	2.9(1)
C3	0.779(1)	0.4474(3)	0.3396(3)	2.8(1)
C4	0.795(1)	0.5450(3)	0.3393(3)	3.3(2)
C5	0.856(1)	0.6058(3)	0.1755(3)	3.5(2)
C6	0.786(1)	0.6888(3)	0.1705(4)	4.1(2)
C7	0.890(1)	0.7480(4)	0.1166(4)	5.0(2)
C8	1.065(1)	0.7247(4)	0.0674(4)	5.0(2)
C9	1.128(1)	0.6427(5)	0.0698(5)	5.4(2)
C10	1.028(1)	0.5818(4)	0.1236(4)	4.7(2)
C11	0.655(1)	0.3893(3)	0.1822(3)	3.1(1)
C12	0.492(1)	0.4163(4)	0.1305(4)	4.6(2)
C13	0.367(1)	0.3582(5)	0.0829(4)	6.0(2)
C14	0.410(1)	0.2726(4)	0.0865(4)	4.8(2)
C15	0.577(1)	0.2456(4)	0.1360(4)	4.2(2)
C16	0.698(1)	0.3037(4)	0.1830(4)	3.8(2)
C17	0.572(1)	0.4129(3)	0.3767(3)	4.0(2)
C18	1.006(1)	0.5785(4)	0.3595(3)	4.1(2)
O1	0.5632(9)	0.4208(2)	0.4731(2)	5.4(1)
O2	1.048(1)	0.5738(3)	0.4537(3)	6.9(1)
1,1,2,2-Tetramethyl-*trans*-3,4-diphenylcyclobutane (**6**)				
C1	−0.2758(5)	0.1093(3)	0.5525(2)	4.2(1)
C2	−0.1927(5)	0.0883(3)	0.6101(2)	4.1(1)
C3	−0.0714(5)	0.1374(3)	0.5654(2)	3.4(1)
C4	−0.1742(5)	0.1798(3)	0.5314(2)	3.9(1)
C5	0.0246(5)	0.1815(3)	0.6006(2)	3.7(1)
C6	0.1134(6)	0.1388(3)	0.6326(3)	4.6(1)
C7	0.2013(6)	0.1769(4)	0.6670(3)	6.0(2)
C8	0.2042(6)	0.2585(4)	0.6694(3)	6.7(2)
C9	0.1201(7)	0.3025(3)	0.6378(3)	6.1(2)
C10	0.0295(6)	0.2644(3)	0.6026(3)	4.9(1)
C11	−0.1328(5)	0.2102(3)	0.4567(2)	3.7(1)
C12	−0.2327(5)	0.2363(3)	0.4229(3)	4.5(1)
C13	−0.1947(6)	0.2625(3)	0.3543(3)	5.1(1)
C14	−0.0602(6)	0.2651(3)	0.3203(3)	5.4(1)
C15	0.0395(6)	0.2411(3)	0.3533(3)	5.2(1)
C16	0.0021(5)	0.2130(3)	0.4214(2)	4.5(1)
C17	−0.2594(6)	0.0473(3)	0.4951(3)	5.9(1)
C18	−0.4258(6)	0.1278(4)	0.5774(3)	6.6(2)
C19	−0.2521(6)	0.1268(3)	0.6798(3)	5.3(1)
C20	−0.1649(6)	0.0014(3)	0.6226(3)	5.5(1)

a) $B_{\mathrm{eq}}=4/3\sum_i\sum_j B_{ij}a_i a_j$.

Table 3. Bond Distances, Bond Angles, and Dihedral Angles (ϕ) of the Cyclobutane Rings and Torsional Angles (θ)[a]

Compd.	Bond distance/Å	Bond angle/deg	ϕ/deg	θ/deg
1	C_A-C_B 1.576(9)	C_A-C_B-C_C 88.4(6)	18	73.1 (C8-C9-C4-C3)
	C_A-C_D 1.573(10)	C_B-C_C-C_D 90.0(6)		74.6 (C14-C15-C3-C4)
	C_B-C_C 1.581(10)	C_C-C_D-C_A 89.5(7)		
	C_C-C_D 1.551(10)	C_D-C_A-C_B 89.4(6)		
2	C_A-C_B 1.57(2)	C_A-C_B-C_C 88(1)	3	79.9 (C8-C9-C4-C3)
	C_A-C_D 1.56(2)	C_B-C_C-C_D 91(1)		78.5 (C11-C16-C2-C1)
	C_B-C_C 1.57(2)	C_C-C_D-C_A 90(1)		
	C_C-C_D 1.54(2)	C_D-C_A-C_B 90.8(9)		
3	C_A-C_B 1.575(6)	C_A-C_B-C_C 87.9(3)	22	77.4 (C12-C11-C1-C4)
	C_A-C_D 1.578(6)	C_B-C_C-C_D 90.9(3)		81.5 (C10-C5-C4-C1)
	C_B-C_C 1.551(6)	C_C-C_D-C_A 87.0(3)		
	C_C-C_D 1.574(6)	C_D-C_A-C_B 89.9(3)		
4	C_A-C_B 1.548(8)	C_A-C_B-C_C 89.4(5)	28	89.5 (C6-C5-C1-C2)
	C_A-C_D 1.531(9)	C_B-C_C-C_D 87.9(5)		86.5 (C16-C11-C2-C1)
	C_B-C_C 1.514(8)	C_C-C_D-C_A 89.9(5)		
	C_C-C_D 1.517(9)	C_D-C_A-C_B 86.2(5)		
5	C_A-C_B 1.539(6)	C_A-C_B-C_C 89.6(3)	23	8.3 (C10-C5-C1-C2)
	C_A-C_D 1.554(6)	C_B-C_C-C_D 88.3(3)		4.2 (C12-C11-C2-C1)
	C_B-C_C 1.550(6)	C_C-C_D-C_A 89.3(4)		
	C_C-C_D 1.544(6)	C_D-C_A-C_B 88.3(4)		
6	C_A-C_B 1.523(5)	C_A-C_B-C_C 88.4(3)	30	11.3 (C16-C11-C4-C3)
	C_A-C_D 1.549(5)	C_B-C_C-C_D 87.3(3)		2.3 (C10-C5-C3-C4)
	C_B-C_C 1.557(5)	C_C-C_D-C_A 86.3(3)		
	C_C-C_D 1.590(5)	C_D-C_A-C_B 90.0(3)		

a) See Fig. 4.

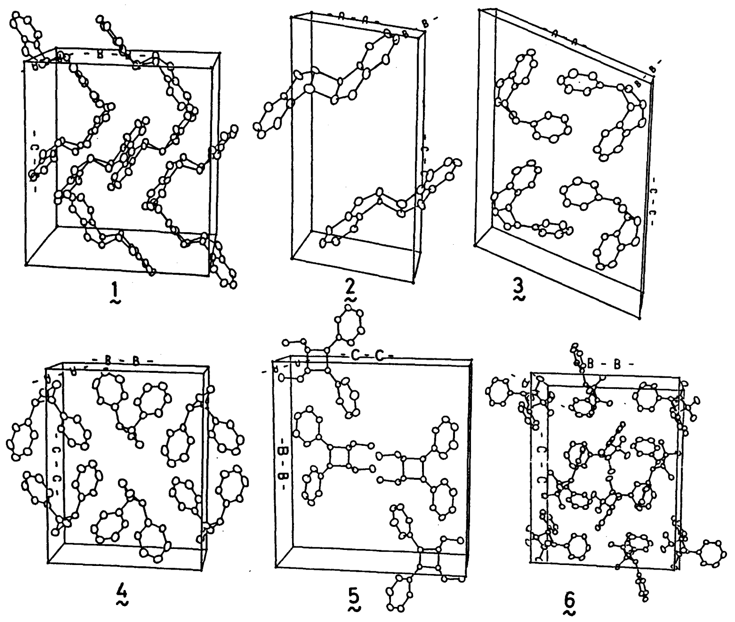


Fig. 2. Crystal-packing diagrams of **1**—**6**.

dihedral angles (ϕ) between the $C_AC_BC_D$ and $C_BC_CC_D$ planes of the cyclobuatne rings, and torsional angles (θ) between the planar ring of the aryl substituent and the plane involving ipso carbon of the aryl group and the C_A-C_B bond. Figure 4 shows the relevant angles, together with notation of the cyclobutane-ring carbon atoms, which are used in further discussion for convenience. These data are shown in Table 3.

The bond distances of the cyclobutane ring of **1**—**3** are slightly longer than the normal distances of monocyclic cyclobutanes (1.52—1.56 Å),[1] perhaps due to the fused tricyclic or bicyclic structure. However, it is important to note that the C_A-C_B bond of **1** and **3** is not unusually longer than the cyclobutane-ring bonds of head-to-tail cyclobutane **2**. The C_B-C_C and C_C-C_D bonds of **4** are relatively short, suggesting a slight distortion of the cyclobutane ring which might arise from steric repulsion between the vicinal phenyl

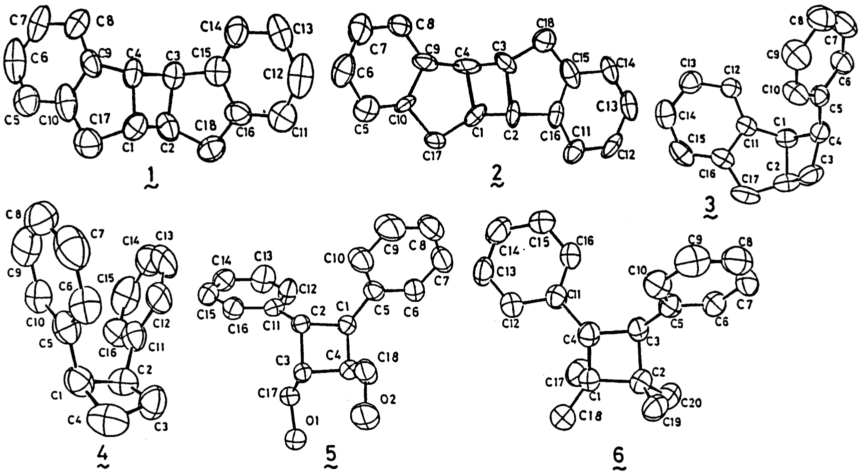


Fig. 3. ORTEP drawing of molecular structures of **1**—**6**.

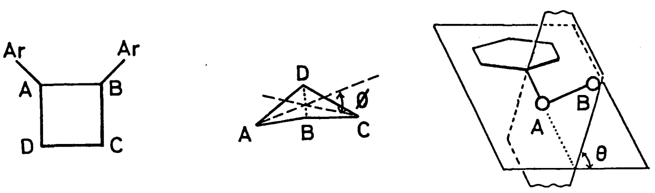


Fig. 4. Notation of each carbon atom of the cyclobutane ring, dihedral angle (ϕ), and torsional angle (θ).

groups in the cis configuration, as shown by the molecular structure in Fig. 1 as well as by molecular models. Similarly, the long C_C-C_D distance of **6** can be attributed to nonbonding interactions between the methyl substituents at C_C and C_D. However, it should be noted that the C_A-C_B distances of **4**—**6** fall within the normal values. The cyclobutane rings of **1**—**6** commonly take puckering forms, in which the $C_AC_BC_D$ and $C_BC_CC_D$ planes meet at the C_B-C_D line with normal dihedral angles (3—30°).$^{1)}$ The bond angles of the cyclobutane rings are also normal, very close to 90°. It is, therefore, appropriate to conclude that these cyclobutanes are not unusually distorted but, rather, relatively normal.

Of particular related significance regarding through-bond coupling is that the θ values are close to 90° in the cases of **1**, **3**, and **4** but very small (2.3—11.3°) in the cases of **5** and **6**. The solid-state conformations of the aryl substituents should be virtually preserved in solution as well, since the rotational motions of the aryl rings are almost frozen by the rigid tricyclic structures of **1** and **2**, and are largely restricted by nonbonding interactions between the phenyl ring and the vicinal cis substituents in **3**—**6**. This is strongly supported by comparisons of the C_A-H chemical shifts in ^{1}H NMR using **1** as a reference compound with an almost fixed conformation. The resonance of C_A-H of **1** appears at δ 3.50, being considerably higher in field than that of **3** (the methine proton of the indan moiety, δ 3.98) and also than that of **4** (PhC-$\underline{H}$, δ 3.92). This is clearly due to shielding of C_A-H by the opposite aryl ring at C_B facing to this proton, while the cis configuration of the two aryl substituents of **3** and **4** prohibits such magnetic anisotropic effects on $C_A(C_B)$-H. The aromatic resonances of **3** and **4** are spread over a wider range of field, δ 6.03—7.8 for **3** and δ 6.61—7.3 for **4** compared with those of **1** (δ 6.8—7.3) and **5**—**8** (δ 6.8—7.4), thus indicating that the aryl rings of **3** and **4** take face-to-face conformations, i.e., $\theta \approx 90°$. On the other hand, the C_A-H resonance of **5** (δ 4.22) is much lower in field than that of **1**, irrespective of similar configurational situations and even lower than that of **4**. This is in line with the solid-state conformation of **6** in Fig. 3, since $C_A(C_B)$-H should be deshielded by the phenyl ring at $C_B(C_A)$. In the case of **6**, however, the deshielding effects of the phenyl ring should be counterbalanced by the shielding effects of the methyl group at $C_D(C_C)$ facing to $C_A(C_B)$-H, whereas one of the geminal ring facing to this group. As a result, **6** reveals a C_A-H(C_B-H) resonance at δ 3.55 and two methyl signals at δ 0.80 and 1.13.

Structure-Dependent Orbital Interactions Associated with Through-Bond Coupling. Figure 5 shows qualitative molecular-orbital diagrams of 1,2-diphenylcyclobutane with $\theta = 90°$ using Salem's σ orbital of cyclobutane$^{2a)}$ and combinations of the π orbitals of benzene and toluene as the basis-set orbitals, which are symmetric or antisymmetric with respect to two-fold rotation or reflection. As shown in Fig. 6, the π orbitals of "head-to-head" diarylcyclobutanes may interact with the C_A-C_B σ orbitals or with the C_A-C_D and C_B-C_C σ orbitals, depending on the conformations of aryl substituents. The rigid tricyclic structure of **1** or the cis configurations of the vicinal aryl substituents of **3** and **4** almost freeze the conformations of the aryl groups favorable to maximum orbital overlapping of the π orbitals with the C_A-C_B σ orbitals, as demonstrated by the observed

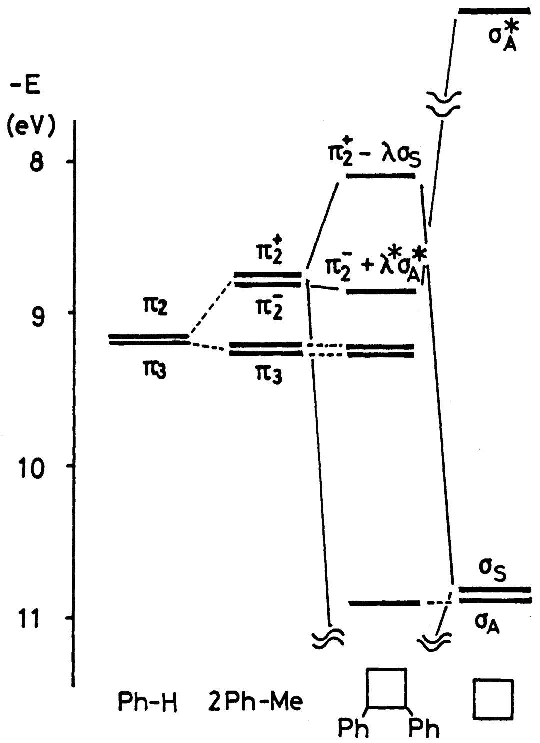


Fig. 5. Schematic molecular-orbital diagrams of 1,2-diphenylcyclobutane with θ=90°; the energy levels of the isolated π and σ orbitals are those of benzene, toluene, and parent cyclobutane, whereas that of $\pi_2^+ - \lambda\sigma_S$ is estimated from the reported ionization potential of *trans*-1,2-diphenylcyclobutane.

torsional angles (θ) being very close to 90°. In the cases of these cyclobutanes (group (i)), the symmetric π_2 combination (π_2^+) can interact with symmetric σ_S to give the highest-occupied molecular orbital (HOMO), $\pi_2^+ - \lambda\sigma_S$, whereas the antisymmetric combination (π_2^-) may interact with σ_A^* to give a bonding MO, $\pi_2^- + \lambda^*\sigma_A^*$.[11,12)]

On the other hand, the θ values of **5** and **6** (group (ii)) are very small (2.3—11.3 °) because of steric repulsion between the phenyl groups and the vicinal methyl or hydroxymethyl substituents in the cis configuration, demonstrating that the π orbitals can not overlap with the orthogonal C_A-C_B σ orbitals but can do so favorably with the C_A-C_D and C_B-C_C σ orbitals. Such restricted conformations should allow only π_2^--σ_A and π_2^+-σ_S^* interactions, which are certainly ineffective to through-bond coupling. Similarly, the orbital interactions of head-to-tail cyclobutane **2** are ineffective regarding through-bond coupling.

Probably, **7** falls in group (i), since the phenyl substituents can take conformations of $\theta \approx 90°$ without steric repulsion. In this regard, it should be noted that the chemical shift of C_A-H (C_B-H) of **7** (δ 3.50) in the ^{1}H NMR spectrum is the same as that of **1**, but higher in field than that of **4**. This suggests that the phenyl rings of **7** assume stable conformations similar to the structure of **1**. On the other hand, **8** belongs to group (ii), as indicated by the C_A-H (C_B-H) chemical shift (δ 4.10) which is very similar to that of **5** (δ 4.22), but lower in field than that of **1**.

Since the reported ionization potential of **7** (8.2 eV)[19)] is considerably lower than those of alkylbenzenes (8.7—8.8 eV),[20,21)] through-bond coupling substantially occurs in group (i) cyclobutanes, i.e., $\lambda > 0$. Furthermore, the group (i) cyclobutanes show oxidation waves in cyclic voltammetry at considerably lower potentials than the others; the observed half-peak oxidation potentials ($E^{ox}_{p/2}$ vs. Ag/AgNO$_3$ in CH$_3$CN) are 1.32 V for **1**, 1.29 V for **4**, and 1.33 V for **7** compared with 1.49 V for **2**, with 1.53 V for **6**, and with 1.63 V for **8**.[3,5)] Although all the cyclobutanes reveal irreversible waves in cyclic voltammetry, the irreversible oxidation potentials would be linearly correlated with the energy levels of the HOMO's of the cyclobutanes, as demonstrated for the oxidation potentials of

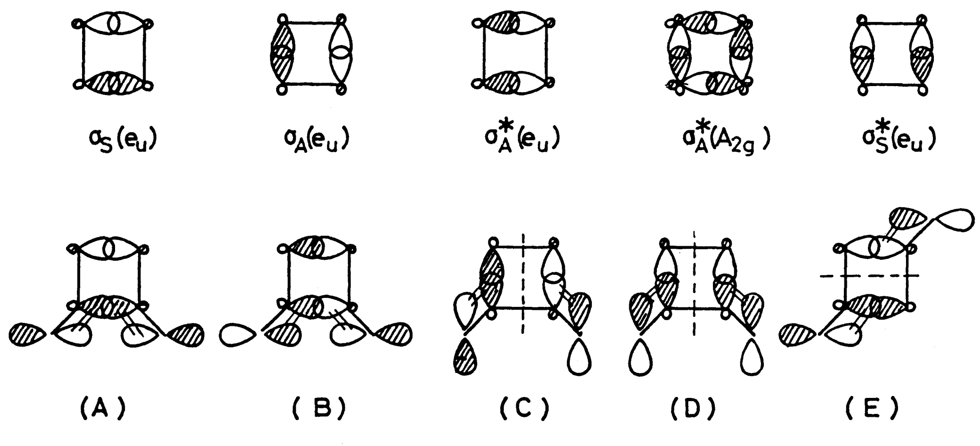


Fig. 6. Top: Salem's σ and σ^* orbitals of cyclobutane. Bottom: (A) π_2^+-σ_S and (B) π_2^--σ_A^* interactions in "head-to-head" cyclobutanes with $\theta \approx 90°$; (C) π_2^--σ_A and (D) π_2^+-σ_S^* interactions in "head-to-head" cyclobutanes with $\theta \approx 0°$ which are ineffective to through-bond coupling; (E) π-σ interactions in "head-to-tail" cyclobutane **2** which are ineffective to through-bond coupling.

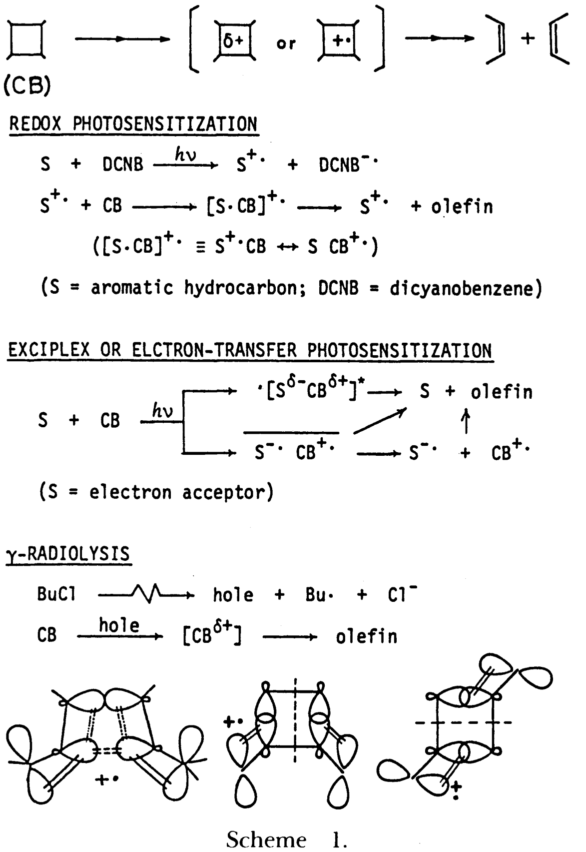
homoleptic alkylmetals and various organic compounds.[22] It might, thereforee, be reasonable to conclude that the π_2 orbitals can significantly couple through interactions with σ_S for the group (i) cyclobutanes while through-bond coupling of π_2 is negligible or inefficient in the other cases, as predicted.

In cases of the group (i) cyclobutanes, the π orbitals may again couple through π_2^--σ_A^* interactions to result in a mixing of the σ^* character in a bonding MO which should bring about a specific elongation of the C_A-C_B bond.[13,14] However, the C_A-C_B bond is normal in the case of **4** or not particularly longer in the cases of **1** and **3** than the other bonds nor than the cyclobutane-ring bonds of **2**. This indicates that π_2^--σ_A^* interactions are not important below room temperature, i.e., $\lambda^* \approx 0$. This is again true for the group (ii) cyclobutanes, as demonstrated by the observed cyclobutane-ring distances. Presumably, the energy levels of σ^*'s are too high for appreciable π-σ^* interactions to occur without any vibrational activation of the relevant σ bond. However, such orbital interactions should play important roles in the transition states of the thermal ring-splitting reactions where σ bonds are vibrationally perturbed (vide infra).

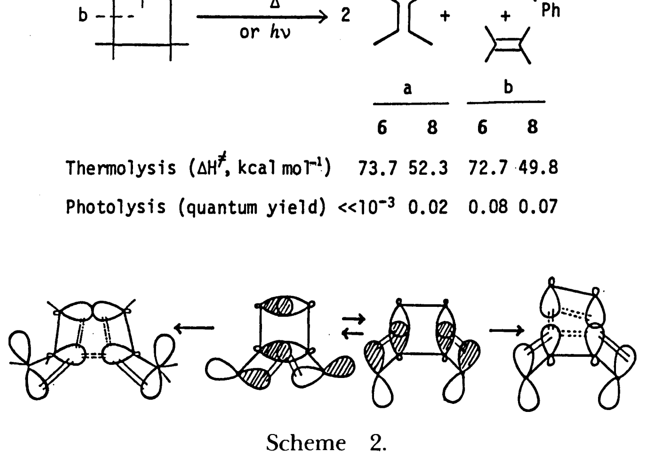
Implications of Through-Bond Coupling in Bond-Cleavage Reactions. The selective C_A-C_B bond cleavage of the group (i) cyclobutanes is effected by redox photosensitization,[3] by exciplex[5] or electron-transfer[6] photosensitization with electron acceptors, and by γ-radiolysis in butyl chloride,[8] giving the corresponding olefins in most cases, as shown in Scheme 1. By contrast, no chemical change of the other cyclobutanes occurs at all by these reactions. The different chemical behavior of the diarylcyclobutanes is certainly in parallel with capabilities of the π-electron systems in coupling through the cyclobutane-ring σ framework.

A key chemical event in the reactions shown in Scheme 1 is the population of a positive charge on the cyclobutanes by charge resonance with a cation radical species and by charge-transfer interactions with or electron transfer to an excited-state electron acceptor. The positive charge population on the group (i) cyclobutanes should be delocalized over the π_2-σ_S-π_2 orbital array, thus leading to decreases in both the C_A-C_B bonding character and the C_A-C_D (C_B-C_C) antibonding character of σ_S, resulting in both a weakening of the C_A-C_B bond and a shortening of the C_A-C_D and C_B-C_C bonds.[23] This is the driving force for the selective bond cleavage of the group (i) cyclobutanes. In the cases of the other cyclobutanes, however, the positive charge should be mostly localized on the isolated-π_2 orbital to cause only minor or slight perturbation of the cyclobutane-ring σ framework, since through-bond coupling is much weaker or disallowed to occur. This is clearly ineffective to bond-cleavage reactions.

Thermal ring-splitting reactions of the "head-to-head" cyclobutanes reveal interesting features in regiochemistry as well as in reactivities, depending on the stable conformations associated with different orbital interactions (Scheme 2).[9] Exclusive or dominant C_A-C_B cleavage occurs upon heating **1**, **4**, or **7** to give



Scheme 1.



	1	**4**	**7**
Thermolysis ($\Delta H^{\neq}$, kcal mol^{-1})	38.6	40.0	39.8
Photolysis (quantum yield)	0.47	0.14	0.14

	a		b	
	6	**8**	**6**	**8**
Thermolysis ($\Delta H^{\neq}$, kcal mol^{-1})	73.7	52.3	72.7	49.8
Photolysis (quantum yield)	$\ll 10^{-3}$	0.02	0.08	0.07

Scheme 2.

indene or styrene with activation enthalpies of ca. 40 kcal mol^{-1},[9,24] while **6** and **8** undergo nonselective cleavages of both the C_A–C_B and C_A–C_D bonds with higher activation enthalpies (50—74 kcal mol^{-1}).[9] These observations can be interpreted in terms of conformation-controlled π-σ^* interactions.

Although π-σ^* interactions are negligeble below room temperature, extensive vibrations at elevated temperatures bring about a skeletal distortion of the cyclobutane ring, which should perturb the σ^* levels to allow π-σ^* interactions. Since mixing of the $\sigma_A{}^*$ character by $\pi_2{}^-$-$\sigma_A{}^*$ interactions is inherently more efficient than that of the $\sigma_S{}^*$ character by $\pi_2{}^+$-$\sigma_S{}^*$ interactions, the activation barriers for the C_A–C_B cleavage should be lower than those for the C_A–C_D (C_B–C_C) cleavage unless the relevant orbital interactions are sterically inhibited. Consequently, the C_A–C_B bond is selectively cleaved in cases of group (i) cyclobutanes where $\pi_2{}^-$-$\sigma_A{}^*$ interactions are coformationally allowed. On the other hand, nonbonding interactions between the phenyl and the methyl substituents in **6** and **8** inhibit the phenyl rings from taking conformations for $\pi_2{}^-$-$\sigma_A{}^*$ interactions, thus imposing additional rotational barriers for the C_A–C_B cleavage. This might be the reason why the thermal reactions of **6** and **8** nonselectively occur with higher activation barriers.

The above arguments imply that the effects of through-bond coupling are not static but, rather, dynamic in nature in the control of stereochemical reaction courses in the ring splitting of the diarylcyclobutanes. This is more explicitly shown in photochemistry. The absorption and fluorescence spectra of the cyclobutanes are essentialy identical with those of indan or toluene, independently of the different conformations of the aryl groups,[7] thus demonstrating that the spectroscopic ground and excited singlet states of the cyclobutanes are the same as those of the isolated π chromophores with slight electronic perturbation. Nevertheless, both regioselectivities and efficiencies in the photolytic ring-cleavage reactions are apparently controlled by different orbital interactions, depending on the restricted stable conformations,[7,25] through π^*-σ^* interactions should be taken into consideration when considering the photochemistry.

Conclusion

Among the molecular-structure parameters of the "head-to-head" diarylcyclobutanes which have been determined by X-ray crystallographic analyses, torsional angles (θ) between the aryl ring and the ipso C–C_A–C_B plane are directly related to the different reactivities of the group (i) and group (ii) cyclobutanes in various types of ring-splitting reactions. With $\theta \approx 90°$, through-bond coupling can occur by π-σ_S interactions to give the HOMO and by π-$\sigma_A{}^*$ interactions which result in the mixing of the $\sigma_A{}^*$ character in a bonding MO. On the other hand, restricted conformations of the aryl groups with $\theta \approx 0°$ allow only π-σ_A and π-$\sigma_S{}^*$ interactions which are ineffective to through-bond coupling. The efficient regioselective cleavage of the C_A–C_B bond of the group (i) cyclobutanes can, thus, be interpreted in terms of the delocalization of a positive charge over the π-$C_A(\sigma)$-$C_B(\sigma)$-π orbital array upon partial or complete removal of an electron, in terms of stabilization of the transition state of thermal reaction due to mixing of $\sigma_A{}^*$ character at elevated temperature, and in terms of π^*-$\sigma_A{}^*$ interactions in direct photolysis. Such effects of through-bond coupling might not be effective regarding the bond-cleavage reactions of group (ii) cyclobutanes. The through-bond coupling concept might provide a general rationale for interpreting the steric control of chemical reaction courses in the cleavage of a C–C bond with vicinal π or n substituents.

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