The Crystal and Molecular Structures of 1,1-Dibromo-*trans*-2,3-diphenylcyclopropane and 1,1-Dibromo-*trans*-2,3-bis(4′-nitrophenyl)cyclopropane. The Effects of Halogen and Phenyl Substituents on Cyclopropane Geometries

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Abstract: The structures of 1,1-dibromo-*trans*-2,3-diphenylcyclopropane (**1**) and 1,1-dibromo-*trans*-2,3-bis(4′-nitrophenyl)-cyclopropane (**2**) have been determined by conventional x-ray crystallographic techniques. The cell constants for **1** are a = 15.150 (4), b = 7.180 (2), c = 12.405 (5) Å, and β = 90.87 (1)°; the space group is $C_{2h}{}^6$-$I2/c$. The cell constants for **2** are a = 15.613 (3), b = 13.623 (2), and c = 7.359 (1) Å; the space group is $D_{2h}{}^6$-$Pnna$. The structures of **1** and **2** were refined by full-matrix least-squares techniques to conventional R indices of 0.028 and 0.035, respectively. Both cyclopropanes have crystallographically imposed C_2 symmetry. The cyclopropane rings in both are symmetrical with average ring bond lengths of 1.516 Å. No large substituent effects are observable for bromine or phenyl groups. The nitrophenyl-substituted cyclopropane ring exhibits exactly the same geometry as the phenyl-substituted cyclopropane. It is thus apparent that electron withdrawal by phenyl substituents is unimportant. A comparison of these and other known cyclopropane structures is made and a discussion of cyclopropane substituent effects with respect to both molecular orbital and hybridization schemes is presented.

The cyclopropane ring has continued to be the object of both synthetic and theoretical interest. Much effort has been expended in surveying the electronic nature of cyclopropane through reaction kinetics, molecular orbital theory, and structural studies. Of particular interest is the comparison between olefins and cyclopropanes. Both have the ability to stabilize carbonium ions and to interact in a conjugative fashion with other π centers. A striking difference between them is the inability of cyclopropanes to transmit σ or π substituent effects.

In an effort to assess the effect of substituents on cyclopropane geometries we began a study of substituted cyclopropanes with 1,1-dihalo-2,2-diphenylcyclopropanes.[1] The previously observed inductive effect of halogen substituents[2] was used to explain the short average cyclopropane bond length. In addition, *gem*-diphenyl substitution caused changes in cyclopropane geometry which appeared inconsistent with traditional molecular orbital theory.

In order to study the geometries of phenyl-substituted cyclopropanes in which the phenyl groups are allowed free rotation, 1,1-dibromo-*trans*-2,3-diphenylcyclopropane, (**1**) and 1,1-dibromo-*trans*-2,3-bis(4′-nitrophenyl)cyclopropane (**2**) were prepared and their crystal and molecular structures are reported here.

Experimental Section

Synthesis of (±)-1,1-Dibromo-*trans*-2,3-diphenylcyclopropane (1). The synthesis of **1** was performed as reported in the literature.[3] Crystals suitable for x-ray investigation were obtained by slow cooling of a 5:1 pentane/diethyl ether solution of the cyclopropane to −78 °C.

Synthesis of (±)-1,1-Dibromo-*trans*-2,3-bis(4′-nitrophenyl)cyclopropane (2). A variation of the Seyferth procedure for preparing dihalocyclopropanes was employed in the synthesis of **2**.[4] Owing to the insolubility of *trans*-4,4′-dinitrostilbene in solvents typically used with Seyferth's reagents, nitrobenzene was investigated, and subsequently employed. Into a 100-mL, three-necked flask, fitted with a magnetic stirring bar, condenser, and nitrogen bubbler, was placed 40 mL of nitrobenzene and 0.5 g (1.9 mmol) of *trans*-4,4′-dinitrostilbene. The mixture was heated to 80 °C, at which point the stilbene almost completely dissolved. A solution of 2.5 g (7.0 mmol) of phenyl(tribromomethyl)mercury in 15 mL of nitrobenzene was added slowly over 30 min. The mixture was stirred at 80 °C for 4 h and cooled. An equal volume of benzene was added and the solution filtered. The benzene and nitrobenzene were removed by vacuum distillation. The residue was triturated with ether and the solids filtered. The ether solution was evaporated and the yellow solid was chromatographed on 50 g of neutral alumina. The column was eluted with mixtures of benzene in hexane (250 mL of each: 5, 10, 60, 100%) and finally with 250 mL of 10% acetone in benzene. In the last fraction a small quantity of yellow solid (<50 mg) was obtained. The solid was recrystallized from ether to give dark yellow crystals, mp 180–182 °C: NMR ($CHCl_3$, δ rel to Me_4Si) 8.32 (4 H, doublet, J = 9 Hz), 7.58 (4 H, doublet, J = 9 Hz), 3.40 (2 H, singlet). Repeated recrystallization from ether provided crystals of suitable quality for x-ray diffraction work.

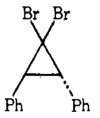
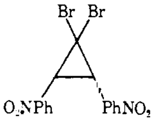
Data Collection and Structure Solution for (±)-1,1-Dibromo-*trans*-2,3-diphenylcyclopropane (1). Preliminary film work suggested the monoclinic space group $I2/c$ (an alternative setting of $C_{2h}{}^6$-$C2/c$, chosen so that $\beta \sim 90°$) or Ic. Lattice parameters (a = 15.150 (4), b = 7.180 (2), c = 12.405 (5) Å, β = 90.87 (1)°) were determined from the least-squares analysis of the setting angles of 16 reflections in the range $35 < 2\theta < 40°$, which had been centered on a FACS-I diffractometer using Mo $K\alpha_1$ radiation (λ 0.709 30 Å) monochromatized from the (002) face of a highly mosaic graphite crystal.[5] Crystal and physical data are listed in Table I.

Intensity data were collected on a FACS-I automatic four-circle diffractometer using monochromated Mo $K\alpha_1$ radiation. The radiation was post-filtered through a 0.025-mm nickel filter to remove fluorescence from bromine. This filtering reduced the background by a factor of 10 and the peak intensity by a factor of 3. The data were collected in shells of 2θ by the θ–2θ technique to a limit of 55° using a scan speed of 2°/min. If the observed intensity was $<3\sigma$, the reflection was rescanned and each background recounted for twice its original counting time and the results of the two scans and two background counts were combined. The seven standards monitored every 100 reflections showed only statistical variations. Details concerning data collection are found in Table I. The methods used in data collection have been reported previously.[1]

The data were corrected for Lorentz and polarization effects and for absorption (μ for Mo $K\alpha_1$ = 59.3 cm^{-1}) using Gaussian integration.[6] A total of 1267 unique data with $F_o{}^2 > 3\sigma(F_o{}^2)$ was used in refinements based on F_o.

The structure was solved by locating the unique bromine atom on a Patterson map, followed by application of successive least-squares and difference Fourier calculations. In this way all atoms, including hydrogen atoms, were located. This justifies the assumption that $I2/c$, rather than Ic, is the correct space group. Full-matrix least-squares techniques were used in refinement. Bromine and carbon atoms were

Table I. Crystal and Physical Data. Data Collection, and Refinement Results for 1,1-Dibromo-*trans*-2,3-diphenylcyclopropane (1) and Its *p*-Nitro Analogue (2)

	 1	 2
Space group	$C_{2h}{}^6$-$I2/c$	$D_{2h}{}^6$-$Pnna$
Z	4	4
Imposed symmetry	C_2	C_2
Cell parameters	a = 15.150 (4) Å b = 7.180 (2) Å c = 12.405 (5) Å β = 90.87 (1)°	15.613 (3) Å 13.623 (2) Å 7.359 (1) Å
Density (calcd), g/cm^3	1.73	1.87
Density (meas), g/cm^3		1.89 (1)
Dimensions of data crystal (along crystal axes), mm	0.38 × 0.47 × 1.02 colorless prism	0.23 × 0.58 × 0.34 yellow prism
Data collection range	2° ⩽ 2θ ⩽ 55° (Mo Kα)	4°⩽ 2θ ⩽ 160° (Cu Kα)
Data collected	$\pm h, k \geqslant 0, l \leqslant 0$	$h, k, l \geqslant 0$
Scan range	1° below Kα_1 to 1° above Kα_2	0.4° below Kα_1 to 0.4° above Kα_2 for 4° ⩽ 2θ ⩽ 125° 0.4° below Kα_1 to 0.5° above Kα_2 for 125° ⩽ 2θ ⩽ 160°
Scan speed, deg/min	2	1 for 4° ⩽ 2θ ⩽ 110° 2 for 110°⩽ 2θ ⩽ 160°
Takeoff angle, deg	3.3	3.1
Aperture, 32 cm from crystal, mm	4.7 horiz 2.6 vert	2.0 horiz 2.3 vert
Background counting times,[a] s	10, 2θ ⩽ 50° 20, 2θ > 50°	10, 2θ ⩽ 110° 20, 2θ > 110°
Agreement indices[b]	R = 0.028 R_w = 0.038	R = 0.035 R_w = 0.062
Standard deviation of observation of unit weight, electrons	1.27 for 103 variables and 1267 data	2.30 for 126 variables and 1399 data

[a] These times are for unrescanned reflections. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o{}^2)^{1/2}$

Table III. Positional and Thermal Parameters for the Atoms of 1,1-Dibromo-*trans*-2,3-diphenylcyclopropane

ATOM	X	Y	Z	B11 OR B, Å^2	B22	B33	B12	B13	B23
BR	0.02927(2)	0.12425(5)	0.12794(3)	5.09(2)	21.80(9)	7.34(3)	0.36(3)	1.01(2)	-3.61(4)
C(1)	0	0.2732(6)	1/4	3.3(2)	17.7(9)	4.4(3)	0	0.2(2)	0
C(2)	0.0348(2)	0.4553(4)	0.2676(3)	3.5(1)	17.7(6)	4.2(2)	-0.5(2)	-0.1(1)	-0.2(3)
C(3)	0.1204(2)	0.5203(4)	0.1970(2)	4.4(1)	14.4(6)	5.4(2)	-0.5(2)	0.7(1)	-1.1(3)
C(4)	0.2071(2)	0.4883(5)	0.2287(3)	4.4(2)	18.8(7)	7.7(3)	0.5(3)	0.6(2)	1.1(4)
C(5)	0.2761(2)	0.5521(6)	0.1659(4)	3.8(2)	25.7(9)	10.2(4)	0.0(3)	1.2(2)	-2.4(5)
C(6)	0.2590(3)	0.6498(6)	0.0737(4)	5.3(2)	25.6(10)	9.1(3)	-2.3(4)	3.2(2)	-2.3(5)
C(7)	0.1740(3)	0.6834(6)	0.0419(3)	6.6(2)	23.9(9)	6.5(3)	-1.7(3)	1.3(2)	2.4(4)
C(8)	0.1049(2)	0.6191(5)	0.1029(3)	4.8(2)	22.1(8)	6.5(2)	-0.5(3)	0.7(2)	1.8(4)
H(2)	0.057(2)	0.474(4)	0.337(2)	2.2(6)					
H(4)	0.216(2)	0.424(5)	0.285(3)	4.8(9)					
H(5)	0.326(3)	0.572(7)	0.200(4)	6.(1)					
H(6)	0.301(3)	0.688(6)	0.033(4)	7.(1)					
H(7)	0.156(3)	0.751(7)	-0.014(4)	6.(1)					
H(8)	0.043(2)	0.641(4)	0.081(3)	3.8(8)					

[a] Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables. [b] The form of the anisotropic thermal ellipsoid is: $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$. The quantities given in the table are the thermal coefficients × 10^3.

refined anisotropically, hydrogen atoms isotropically. The effects of anomalous dispersion were included for bromine. The results of these refinements are given in Table I.

Table II lists the values of 40$|F_o|$ and 40$|F_c|$ (in electrons) for **1**.[7] Table III lists the values of the atomic parameters and their estimated standard deviations. The root-mean-square amplitudes of vibration for the nonhydrogen atoms are found in Table IV.

Data Collection and Structure Solution for (±)-1,1-Dibromo-*trans*-2,3-bis(4′-nitrophenyl)cyclopropane (2). Precession and Weissenberg photography showed that **2** crystallizes in space group $D_{2h}{}^6$-$Pnna$ of the orthorhombic system. Lattice parameters (a = 15.615 (3), b = 13.623 (2), c = 7.359 (1) Å) were determined from the least-squares analysis of the setting angles of 16 reflections in the range of 55 ≤ 2θ ≤ 80°, which had been centered on a FACS-1 diffractometer using Cu Kα_1 radiation (λ 1.540 562 Å) prefiltered with nickel foil.

Intensity data for **2** were collected using Cu Kα radiation. The data were collected in the θ–2θ scan mode in shells of 2θ to a limit of 160°. Data in the range 4–125° were collected in the bisecting mode, those between 125 and 160° in the parallel mode. In the range 4–125°, the rescan option used for **1** was employed. In the range 125–160°, the peak was rescanned as before, but the backgrounds were recounted

Table IV. Root-Mean-Square Amplitudes of Vibration (Å)

	1			2		
Atom	Min	Int	Max	Min	Int	Max
Br	0.1945 (6)	0.2456 (5)	0.2736 (5)	0.2318 (7)	0.2634 (6)	0.3401 (7)
O(1)				0.212 (3)	0.307 (4)	0.336 (4)
O(2)				0.230 (4)	0.291 (4)	0.367 (4)
N				0.223 (4)	0.227 (3)	0.280 (4)
C(1)	0.185 (5)	0.197 (5)	0.215 (5)	0.209 (5)	0.226 (5)	0.268 (6)
C(2)	0.179 (4)	0.201 (4)	0.218 (4)	0.204 (3)	0.237 (4)	0.248 (4)
C(3)	0.185 (4)	0.204 (4)	0.235 (4)	0.203 (3)	0.233 (4)	0.246 (4)
C(4)	0.217 (4)	0.222 (4)	0.253 (4)	0.209 (4)	0.242 (5)	0.250 (4)
C(5)	0.202 (4)	0.249 (5)	0.296 (5)	0.208 (3)	0.250 (4)	0.254 (4)
C(6)	0.189 (4)	0.245 (5)	0.322 (5)	0.204 (4)	0.221 (4)	0.250 (4)
C(7)	0.196 (5)	0.262 (5)	0.287 (5)	0.224 (5)	0.235 (4)	0.308 (5)
C(8)	0.205 (4)	0.243 (4)	0.251 (5)	0.206 (4)	0.239 (4)	0.319 (5)

Table VI. Positional and Thermal Parameters for the Atoms of 1,1-Dibromo-*trans*-2,3-bis(4′nitrophenyl)cyclopropane

ATOM	X[A]	Y	Z	B11[B] OR B,A^2	B22	B33	B12	B13	B23
BR	0.72143(3)	0.38923(4)	0.61592(6)	60.0(3)	98.3(5)	263.(1)	-17.8(2)	-7.0(3)	45.2(4)
O(1)	0.3531(2)	0.3285(2)	0.0233(5)	39.(1)	99.(2)	405.(9)	-7.(1)	-18.(2)	1.(4)
O(2)	0.4377(2)	0.2133(3)	-0.0558(5)	64.(1)	77.(2)	436.(9)	-7.(1)	-37.(3)	-45.(4)
N	0.4235(2)	0.2923(2)	0.0137(4)	48.(1)	63.(2)	225.(6)	-8.(1)	-15.(2)	19.(3)
C(1)	3/4	1/2	0.4713(6)	40.(2)	71.(3)	185.(9)	-10.(2)	0	0
C(2)	0.7038(2)	0.5172(3)	0.2930(5)	34.(1)	63.(2)	216.(7)	-1.(1)	-2.(2)	5.(3)
C(3)	0.6317(2)	0.4547(3)	0.2271(5)	34.(1)	64.(2)	197.(6)	-1.(1)	-1.(2)	1.(3)
C(4)	0.5479(2)	0.4817(3)	0.2655(5)	39.(1)	61.(2)	221.(7)	4.(1)	10.(2)	-3.(3)
C(5)	0.4801(2)	0.4290(3)	0.1972(5)	36.(1)	68.(2)	226.(7)	1.(1)	8.(2)	1.(3)
C(6)	0.4960(2)	0.3482(3)	0.0901(4)	38.(1)	58.(2)	187.(6)	-2.(1)	-11.(2)	15.(3)
C(7)	0.5777(2)	0.3192(3)	0.0511(6)	46.(1)	77.(3)	257.(8)	7.(2)	-9.(3)	-41.(4)
C(8)	0.6459(2)	0.3727(3)	0.1198(6)	35.(1)	88.(3)	274.(9)	6.(1)	-6.(3)	-43.(4)
H(2)	0.691(3)	0.583(4)	0.261(7)	7.(1)					
H(4)	0.534(3)	0.542(4)	0.315(6)	4.(1)					
H(5)	0.422(3)	0.451(3)	0.225(6)	5.2(9)					
H(7)	0.582(3)	0.274(4)	-0.003(6)	5.(1)					
H(8)	0.707(3)	0.349(5)	0.108(7)	8.(1)					

[a] Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables. [b] The form of the anisotropic thermal ellipsoid is: $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$. The quantities given in the table are the thermal coefficients $\times 10^4$.

for only the length of time they had been originally counted. The six standards which were monitored every 100 reflections displayed only statistical variations. Crystal and physical data and details concerning data collection are found in Table I.

The data were corrected for Lorentz and polarization effects and for absorption (μ for Cu Kα = 68.3 cm^{-1}).[6] A total of 1399 unique data with $F_o^2 > 3\sigma(F_o^2)$ was used in the refinements based on F. A Patterson map was used to locate the bromine atom, and subsequent applications of least-squares and difference Fourier calculations revealed the positions of all other atoms, including hydrogen atoms. The bromine, nitrogen, oxygen, and carbon atoms were refined anisotropically and the hydrogen atoms isotropically by full-matrix least-squares techniques. The results of these refinements are given in Table I.

Table V lists the values of $40|F_o|$ and $40|F_c|$ (in electrons) for **2**.[7] Table VI lists the values of the atomic parameters and their estimated standard deviations. The root-mean-square amplitudes of vibration for the heavy atoms are found in Table IV.

Results

The Crystal Structures. The two cyclopropane derivatives crystallize in different space groups (Table I). Since both cyclopropanes were prepared as racemic mixtures, and no spontaneous resolution occurred on crystallization, centric space groups were not excluded and in fact were found. An interesting feature is that in both cases the molecules are located on C_2 axes, one half of the molecule being unique. Both crystal structures are comprised of monomeric units. The shortest intermolecular contacts in the diphenylcyclopropane are H-H interactions, all of which are longer than 2.8 Å. The bis(nitrophenyl)cyclopropane has its shortest contacts between the oxygen atoms of the nitro group and H(2), H(4), and H(8) atoms of other molecules. These distances range from 2.49 to 2.56 Å, approximately the sum of the van der Waals radii. Stereoviews of the unit cell for both diphenyl- and bis(nitrophenyl)cyclopropanes are given in Figures 1 and 2, respectively.

The Molecular Structures. The molecular structures of the two cyclopropanes, in spite of the differences in space groups and phenyl substituents, are nearly identical. The similarity between the two structures can be seen in Figure 3, which shows single molecules of diphenyl- and bis(nitrophenyl)cyclopropane. Identical numbering schemes have been employed in both molecules and are shown in this figure and in Figure 4. Bond distances and angles are given in Table VII.

Rotations of the phenyl rings in the present cyclopropanes are not constrained by ortho interactions. Such constraints occur in *gem*-diphenylcyclopropanes, which comprise a large percentage of the known cyclopropane structures. Of interest is the acute angle between the phenyl ring and the C(1)-C(2′) bond, being 48.5 (2)° for **1** and 52.2 (2)° for **2**. The significance of these angles will be discussed below. The geometries of the phenyl rings are normal, the average bond length being 1.377 (11) Å for **1** and 1.379 (9) Å for **2**. The C(2)-C(3) bond lengths are 1.487 (4) and 1.493 (4) Å for **1** and **2**. In **2**, the nitro group is symmetrical with N-O bond lengths of 1.207 (4) and 1.212 (4) Å. The O-N-O angle of 123.6 (3)° and the dihedral angle between the phenyl ring and the plane of the nitro group (11.4°) are reasonable in comparison with known structures.[8]

Table VII. Intramolecular Bond Distances (Å) and Angles (deg)

	1		2	
	Bond Distances			
C(1)–Br	1.911 (3)		1.900 (3)	
C(1)–C(2)	1.515 (5)	1.516 (5)[a]	1.516 (5)	1.516 (6)
C(2)–C(2')	1.518 (5)		1.517 (6)	
C(2)–C(3)	1.487 (4)		1.493 (4)	
C(3)–C(4)	1.386 (5)	1.377 (11)	1.388 (4)	1.379 (9)
C(3)–C(8)	1.381 (5)		1.385 (5)	
C(4)–C(5)	1.391 (5)		1.376 (5)	
C(5)–C(6)	1.363 (6)		1.375 (6)	
C(6)–C(7)	1.364 (6)		1.366 (5)	
C(7)–C(8)	1.380 (5)		1.386 (5)	
C(2)–H(2)	0.89 (3)		0.95 (5)	
C(4)–H(4)	0.85 (4)	0.89 (5)	0.92 (5)	0.92 (12)
C(5)–H(5)	0.87 (4)		0.97 (4)	
C(6)–H(6)	0.86 (4)			
C(7)–H(7)	0.89 (5)		0.73 (5)	
C(8)–H(8)	0.98 (4)		1.01 (5)	
C(6)–N			1.476 (4)	
N–O(1)			1.207 (4)	1.210 (4)
N–O(2)			1.212 (4)	
	Bond Angles			
C(1)–C(2)–C(2')	59.9 (1)		60.0 (1)	
C(2)–C(1)–C(2')	60.1 (3)		60.1 (3)	
Br–C(1)–Br'	112.0 (2)		111.8 (2)	
Br–C(1)–C(2)	118.8 (1)		119.8 (1)	
Br–C(1)–C(2')	119.1 (1)		118.3 (2)	
C(3)–C(2)–C(1)	123.0 (2)		123.5 (3)	
C(3)–C(2)–C(2')	122.9 (3)		122.7 (4)	
H(2)–C(2)–C(3)	115 (2)		108 (3)	
H(2)–C(2)–C(1)	110 (2)		117 (3)	
H(2)–C(2)–C(2')	115 (2)		119 (3)	
C(4)–C(3)–C(2)	118.8 (3)		119.5 (3)	
C(8)–C(3)–C(2)	122.8 (3)		121.7 (3)	
C(8)–C(3)–C(4)	118.3 (3)	119.8 (9)	118.7 (3)	120.2 (11)
C(3)–C(4)–C(5)	120.1 (4)		120.9 (3)	
C(4)–C(5)–C(6)	120.4 (4)		119.2 (3)	
C(5)–C(6)–C(7)	120.0 (4)		121.4 (3)	
C(6)–C(7)–C(8)	120.2 (4)		119.2 (4)	
C(7)–C(8)–C(3)	121.0 (4)		120.7 (3)	
C(5)–C(6)–N			119.5 (3)	
C(7)–C(6)–N			119.1 (3)	
C(6)–N–O(1)			117.7 (3)	
C(6)–N–O(2)			118.7 (3)	
O(1)–N–O(2)			123.6 (3)	
	Torsion Angle			
C(2')–C(1)–C(2)–C(3)	111.9 (4)		111.5 (5)	
C(1)–C(2')–C(2)–C(3)	112.0 (2)		112.7 (2)	
C(1)–C(2)–C(3)–C(4)	96.5 (4)		93.3 (4)	
C(1)–C(2)–C(3)–C(8)	85.9 (4)		90.3 (4)	
C(2')–C(2)–C(3)–C(4)	169.6 (2)		166.5 (3)	
C(2')–C(2)–C(3)–C(8)	12.8 (4)		17.0 (5)	
C(3)–C(2)–C(2)–C(3)	136.0 (5)		134.6 (5)	
	Dihedral Angle between Planes			
C(1)–C(2)–C(2') C(3)–C(5)–C(7)	60.2 (1)		56.9 (1)	
O(1)–N–O(2) Phenyl ring			11.4	
	Angle between a Plane and Vector			
C(3)–C(5)–C(7) C(1)–C(2')	48.5 (2)		52.2 (2)	

[a] Average value of equivalent bonds. The standard deviation is the larger of that of an individual distance, based on averaging, or of an individual measurement as derived from the inverse matrix.

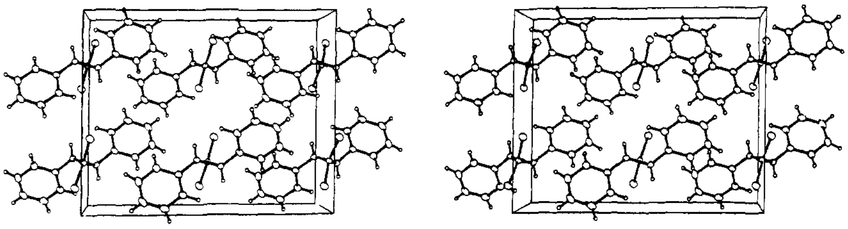


Figure 1. Stereoview of the unit cell of 1,1-dibromo-*trans*-2,3-diphenylcyclopropane. The x axis is horizontal, the z axis is vertical, and the y axis points out of the paper. The ellipsoids represents 20% probability contours. The hydrogen atoms are of arbitrary size.

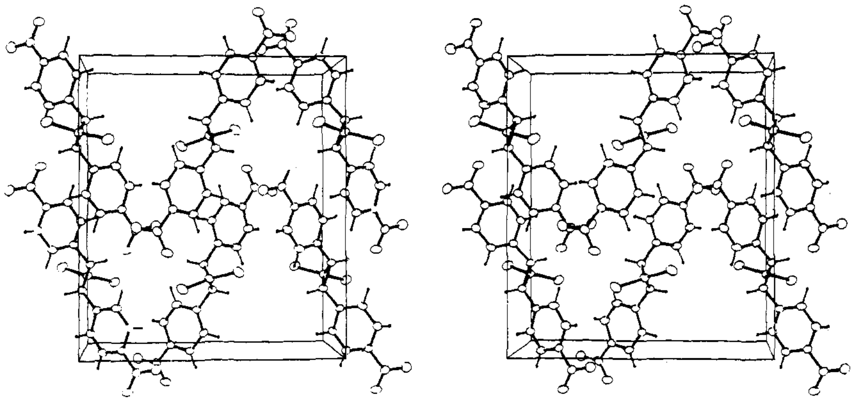


Figure 2. Stereoview of the unit cell of 1,1-dibromo-*trans*-2,3-bis(4′-nitrophenyl)cyclopropane. The y axis is horizontal, the x axis is vertical, and the z axis points into the plane of the paper. The ellipsoids represent 20% probability contours. The hydrogen atoms are of arbitrary size.

The cyclopropane rings in both structures are symmetrical within experimental error. In fact, the range of cyclopropane bond lengths in both structures is less than the standard deviation in any one bond length. The average of the bond lengths for the four unique cyclopropane bonds is 1.516 (3) Å. The bond angles around the rings are all 60° within the limits of error. The structural parameters of greatest interest are shown in Figure 4.

The Br–C(1)–Br angles are identical, being 112.0 (2)° for **1** and 111.8 (2)° for **2**. These angles are slightly larger than the value of 110.7 (2)° found for 1,1-dibromo-2,2-diphenylcyclopropane.[1] The C(1)–Br bond lengths are 1.911 (3) and 1.900 (3) Å for **1** and **2**, respectively; the difference between them is only of marginal statistical significance. The difference can be ascribed in part to differences in thermal motion, as judged by the root-mean-square amplitudes of vibration for the bromine atoms given in Table IV.

All the hydrogen atoms for both structures were found by difference Fourier techniques and their positions and thermal parameters were varied in refinement. The C(2)–H(2) bond lengths are 0.88 (3) Å for **1** and 0.95 (5) Å for **2**, with H(2)–C(2)–C(3) bond angles of 115 (2) and 107 (3)°, respectively. No significance can be attached to these differences.

Discussion

The focal point of this and previous structural studies of substituted cyclopropane structures is the search for bond length trends which agree or disagree with those predicted by molecular orbital theory. It has been shown that there is a significant difference between the geometrical effects of halogen and phenyl substituents. The primary influence of halogens has been ascribed to a σ-withdrawal of electron density from the cyclopropane ring with a concomitant increase in the average ring bond length. Phenyl rings, on the other hand, bring about structural changes consistent with π conjugation, but in compounds which do not impose or obtain the conformation most often implicated for such conjugation.[1]

In an effort to sort out the structural effects ascribable to phenyl rings, the halogen substituents were kept the same and the phenyl rings situated to allow free rotation. In addition, the electronic demand of the phenyl rings, as influenced by the substitution of nitro groups for the para-hydrogen atoms, was altered in an attempt to influence the strength of the phenyl-cyclopropane interaction.

Effect of Halogen Substituents on Cyclopropane Geometries. Three different orbital interactions between halogen substituents and cyclopropanes, based on the Walsh model of cyclopropane, have been used to explain the observed cyclopropyl geometries.[1,2,9,10] They are: (1) σ-withdrawal of electron density from the cyclopropane; (2) donation of electron density from a p orbital of halogen to the $1a_2'$ (all antibonding) orbital of cyclopropane; (3) donation of electron density from a p orbital on halogen to the unfilled $4e'$ cyclopropane orbital of appropriate symmetry. All three interactions serve to lengthen the C(1)–C(2) bond, while the C(2)–C(3) bond is lengthened by (1) and (2), but shortened by (3). These orbitals are shown in Figure 5. The orbitals in Figure 5 are approximate, depicting the principal atomic orbitals at each carbon atom with their approximate relative sizes. The shapes of the antibonding orbitals are also approximate. The symmetry designations for the cyclopropane orbitals are those of cyclopropane. Positions of attachment for substituents are determined by the number of substituents and the orbital involved. Thus, interaction of a cyclopropane with one substituent will take place through the orbitals depicted in Figures 5a,c,e. Similarly, two substituents will interact with a cyclopropane through those orbitals depicted in Figure 5b,d,e. The three perturbations listed above, involving one substituent at a time, will cause qualitatively the same geometric changes regardless of the total number of substituents.

There is great difficulty in explaining known halogenated cyclopropane structures[11-18] in terms of these three orbital interactions. Table VIII collects the structural information on these cyclopropanes. A cursory inspection reveals the lack of any uniform bond lengthening. With the exception of 1,1-

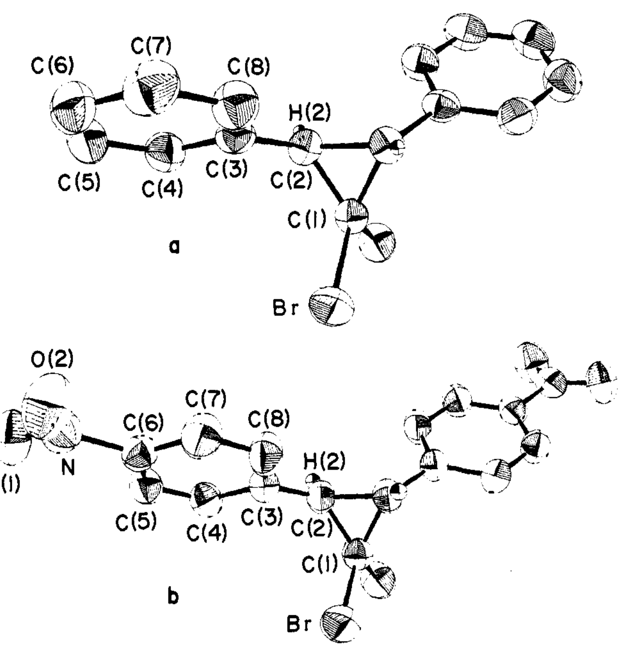


Figure 3. (a) Perspective view of 1,1-dibromo-*trans*-2,3-diphenylcyclopropane (**1**). (b) Perspective view of 1,1-dibromo-*trans*-2,3-bis(4′-nitrophenyl)cyclopropane (**2**). The ellipsoids represent 50% probability contours. The numbering schemes for each compound are given and are equivalent.

dichloro- and 1,1-difluorocyclopropane, the average bond lengths are all reasonably similar to that of cyclopropane. In addition, the bonds in the cyclopropane fragment of a particular compound, with only a few exceptions, do not show a wide range in length, demonstrating that this similarity is not an artifact of the averaging process.

The rationalization of fluorinated cyclopropane structures presents a stern challenge. *cis,cis*-1,2,3-Trifluoro- and hexafluorocyclopropane have C–C bond lengths identical with that in cyclopropane. These structures belie the importance of σ-withdrawal of electron density as a primary source of ring geometry changes. 1,1-Difluorocyclopropane, however, exhibits one of the most remarkable spreads in bond lengths (1.464 (2)–1.553 (1) Å) of any compound with only σ bonds.[14] Of interest is that the changes in bond length are completely *opposite* to those predicted by the orbital interactions cited earlier.[14,15] However, Bernett has been able successfully to rationalize the structures of both cyclopropanes and fluorinated hydrocarbons on the basis of changes in the hybridization of carbon orbitals.[19,20] An increase in the p character of the C–F bonding orbitals of C, as required by Bernett's view of fluorocarbon bonding, would reduce the p character in the C–C ring bonds. In order to maintain the same overlap between the cyclopropane carbon atoms, the internuclear separation would have to decrease. Gillies also observed a similar shortening of the bonds α to fluorine, but did not discuss the origin of this trend.[15] Because the angle between the orbitals on the CF_2 carbon atom used to form the cyclopropane bonds has increased, the C(2)–C(3) bond length should increase. Thus changes in hybridization can be used to predict the direction, if not the unusual magnitude, of the perturbations wrought by *gem*-difluoro substituents.

The chloro- and bromo-substituted cyclopropanes might be expected to exhibit perturbations similar to those of fluorocyclopropanes, only of smaller magnitude. Carbon-carbon bond shortening has been observed α to chlorine and bromine atoms.[21] However, the known chlorocyclopropanes do not follow these trends. Two possible explanations are: (1) there is a superposition of both hybridization changes and opposing orbital interactions; or (2) chlorine and bromine atoms do not cause the extensive hybridization changes ascribed to fluorine substituents.

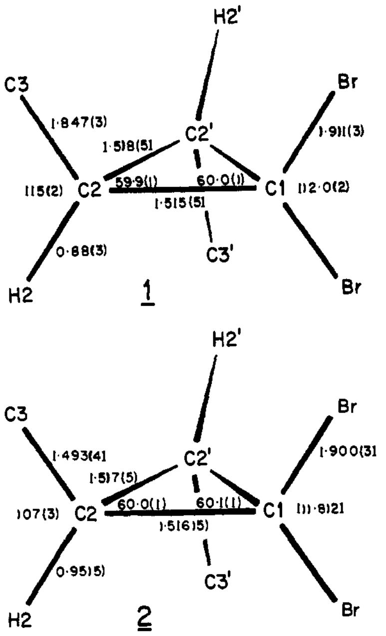


Figure 4. A representation of the cyclopropane rings and attached atoms for **1** and **2**, giving important bond lengths (Å) and angles (deg).

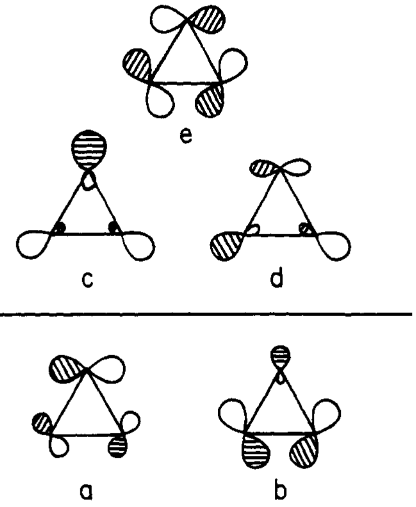
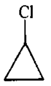
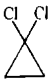
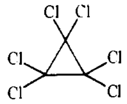
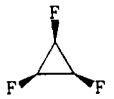
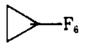
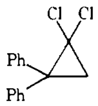
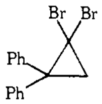
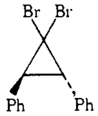
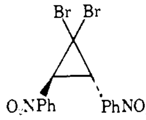
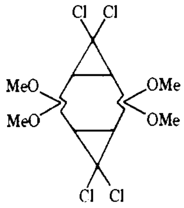
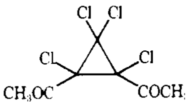


Figure 5. A representation of the two highest occupied and the unoccupied C–C molecular orbitals of cyclopropane. Figures 5a and 5b are the 3e′ orbitals, 5c and 5d the 4e′ orbitals and 5e the 1a$_2$′ orbital. These drawings are atomic orbital approximations of the molecular orbitals found in ref 25, and as such, their nodal properties and not their exact shape are pertinent to the discussion. The symmetry designations are those of cyclopropane.

The structures reported here substantiate the notion that bromine atoms do not significantly alter the bond lengths in cyclopropanes. The average C–C bond length in each structure is indistinguishable from that of cyclopropane. In order to determine if chlorine or bromine substituents cause a detectable change in cyclopropane geometries, more information about cyclopropane structures, with and without attached halogen atoms, must be sought. These studies are already underway.

Effects of Phenyl Substituents on Cyclopropane Geometries. There are two ways in which a π system can interact with the molecular orbitals of cyclopropane. The first is donation of electron density from one of the occupied 3e′ orbitals of cyclopropane, depicted in Figures 5a and 5b, to an unoccupied

Table VIII. Bond Lengths in Halogenated Cyclopropanes

Compd	C(1)–C(2)[a] C(1)–C(3)	C(2)–C(3)	Av bond length	Method[b]	Ref
	1.514 (2)		1.514	m	11
	1.513 (4)	1.515 (1)	1.514	m	12
	1.532 (4)	1.534 (4)	1.533	m	2
	1.513 (9)		1.513	m	13
	1.464 (2)	1.553 (1)	1.494	m	14
	1.507 (1)		1.507	m	15
	1.505 (3)		1.505	e	16
	1.520 (3) 1.490 (3)	1.529 (3)	1.513	x	1
	1.509 (6) 1.477 (6)	1.508 (6)	1.498	x	1
	1.515 (5)	1.518 (6)	1.516	x	This work
	1.516 (5)	1.517 (6)	1.516	x	This work
	1.496 (5) 1.497 (6)	1.546 (5)	1.513	x	17
	1.486 (10) 1.498 (10)	1.516 (10)	1.500	x	18

[a] The cyclopropane rings are numbered counterclockwise beginning at the top carbon atom. [b] Method of structure determination: e, electron diffraction; m, microwave spectroscopy; x, x-ray diffraction.

orbital in the π system.[22,23] The second is donation from one of the occupied levels of the π system to one of the unoccupied 4e′ or 1a$_2$′ orbitals of cyclopropane shown in Figures 5c–e.[24] Cyclopropane donation has most often been invoked in the explanation of the interaction between cyclopropane and a carbonium ion center. To make use of orbital interactions with the 3e′ cyclopropane orbitals, a π system at C(1) must assume the bisected conformation, as shown in Figure 6a. In this way overlap between the π system and the cyclopropane ring is maximized. In the perpendicular orientation, Figure 6b, the p orbitals are mutually perpendicular and there is no overlap between them. When two electron-accepting substituents are bound to vicinal carbon atoms, each with p orbitals adjacent to the cyclopropane ring, the 3e′ orbital in Figure 5b has the proper symmetry to accommodate interactions with both groups. However, the interaction of two π systems with this orbital still requires the bisected conformation for maximum overlap. It is this orbital scheme which is important in consideration of the cyclopropanes under study.

Donation of electron density from a π system to a cyclopropane ring can take place through either the unfilled 4e′ or 1a$_2$′ orbitals. The 1a$_2$′ orbitals, Figure 5e, require the bisected conformation for maximum overlap. However, both the unfilled 4e′ orbitals require the perpendicular conformation. The perpendicular conformation has been used to explain the bond lengths observed in cyclopropylamine.[10,26] It is clear that if the

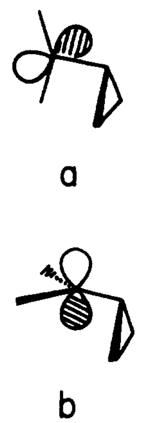


Figure 6. (a) The bisected conformation; (b) the perpendicular conformation.

flow of electrons is from the cyclopropane to the π system, only the bisected conformation allows for overlap of the proper orbitals. However, if the electron flow is from the π system to the cyclopropane, orbitals of proper symmetry are available for overlap from both bisected and perpendicular conformations.

The assumption has been made that the different phenyl ring-cyclopropane interactions can be considered independently. The cyclopropane geometries are then the result of a sum of several terms for each substituent. However, usually one orbital interaction will predominate because of symmetry; attention will be focused on it. In addition, the shapes of the antibonding orbitals[25] are only approximate. However, the calculations should result in orbitals with the correct nodal properties.

It has been proven experimentally that the bisected conformation is far superior to the perpendicular conformation at stabilizing a carbonium ion center.[22,23] However, it is not known if this bisecting conformation represents a true minimum in the potential well and whether this well is steep or flat near its minimum. There is spectroscopic evidence which suggests that either an "off-bisected" minimum or a shallow well (or both) are possible.[27,28]

In order to discuss the geometries of phenylcyclopropanes,[29-35] the numbering systems and certain structural parameters must be defined. Figure 7 displays the features used in Table IX. Carbon atom 2 is always the more highly substituted of the adjacent carbon atoms. The angle θ is the acute angle between the normal to the phenyl ring and the C(2)-C(3) vector. In the bisected conformation the value of θ is 0°; in the perpendicular conformation the value of θ is 90°. In cyclopropanes where the C(1)-C(2) and C(1)-C(3) bond lengths are equal, θ is an accurate measure of the angle between the π system of the benzene ring and the 3e′ orbital depicted in Figure 5a. If these ring bonds are not of equal length, the conformation necessary for maximum overlap is hard to assess. However, θ does not differ significantly from another convenient measure of this interorbital angle.[36] Therefore, θ is used as an appropriate approximation.

From Table IX one can observe the lack of correlation between θ and the C(2)-C(3) bond length. In fact, there is no dependence of any one structural parameter on any other, and that in itself is unexpected. One explanation is that substituents, with the exception of fluoro, cyano, and carbonyl groups, only slightly influence cyclopropane geometries. The bond lengths in a polysubstituted cyclopropane are thus complex sums of electronic, hybridization, and steric constraints. If substituents are held in favorable conformations, the electronic component would be expected to assume greater importance. An illustrative example will be treated below. Any sort of donation-acceptance interaction between substituent and cyclopropane creates a high-energy zwitterionic form which should be an important resonance contributor only for those cases in which the substituent readily donates or accepts electron density. The exceptions noted above certainly obey this criterion. In charged species, such as cyclopropylcarbinyl cations, this restriction is lifted and the conformational angle θ becomes much more critical in determining the stability of the system.

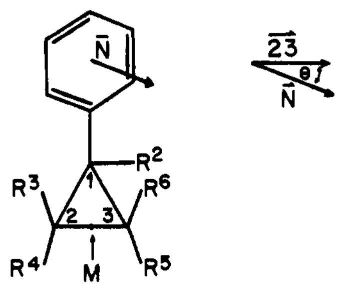


Figure 7. A representation of the geometrical features of phenyl cyclopropanes used in Table IX. $\bar{N}$ is the normal to the benzene ring; M is the midpoint of the C(2)-C(3) bond; θ is the acute angle between $\bar{N}$ and the C(2)-C(3) vector.

A second argument against strong interaction between substituents and a cyclopropane ring in uncharged compounds is the fact that the portion of the orbital depicted in Figure 5a which is centered at C(1) is not a pure p orbital, and thus does not have $D_{\infty h}$ symmetry about atom C(1). Instead, the major portion of the electron density is toward atoms C(2) and C(3). The shape of this orbital as derived from either a MO picture[25] or the hydridization scheme of Bernett[19] demonstrates this fact. Thus, twisting about the C(1)-phenyl bond increases the overlap of the adjacent orbitals on one side of the nodal plane, while decreasing the overlap on the other. Although the total overlap may be a maximum at θ of 0°, one should expect a broad, shallow minimum in the potential well for the interaction of a π system with the 3e′ orbital. Thus, the changes in cyclopropane geometries brought about by the phenyl rings are expected to be small and not very sensitive to the value of θ if electron flow from cyclopropane to phenyl ring is dominant.

An interesting comparison can be made between **1** and 1,1-dibromo-2,2-diphenylcyclopropane. Since the substituents are the same, any inductive effects should be equal. And yet **1** displays a longer (0.02 Å) average cyclopropane bond length. One reason for the short average bond length in 1,1-dibromo-2,2-diphenylcyclopropane is the very short (1.477 Å) C(2)-C(3) bond length. An explanation for this short bond is a π interaction through the unfilled 4e′ cyclopropane orbital shown in Figure 5c. Donation of electron density into this orbital causes a strong bonding interaction between atoms C(2) and C(3). The orbital configuration is shown in Figure 8. Through-bond conjugation of this type has been used to explain unusually long bonds in anthracene photodimers and similar structures.[37] Since the cyclopropane rings in both **1** and **2** are symmetrical with bond lengths almost identical with that of cyclopropane, it is clear that neither phenyl nor p-nitrophenyl substituents actively influence the geometries of cyclopropanes when $\theta \sim 50°$. At θ of 75°, on the other hand, changes in cyclopropane bond lengths occur and lead one to suspect that a major electronic effect of a phenyl ring is donation of electron density into the cyclopropane orbital shown in Figure 5c. It should be noted that a value of $\theta \geq 75°$ is available to both **1** and **2**. Yet the interaction of the phenyl rings with either of the 4e′ orbitals is not strong enough to require this conformation in the crystal structure. Thus the steric constraints which hold 1,1-dibromo-2,2-diphenylcyclopropane in this conformation,

Table IX. Comparison of Phenyl Cyclopropane Structures[a]

Compd R^1	R^2	R^3	R^4	R^5	R^6	θ	C(1)–C(2), Å	C(1)–C(3), Å	C(2)–C(3), Å	C(1)–C(4), Å	Cyclopropane ring bond av	Ref
Ph	Ph	H	$-CH_2-N^+(Et)_2-CH_2-$		H	80.0	1.520	1.514	1.526	1.493	1.520	29
						85.5				1.506		
ClPh	ClPh	Cl	Cl	H	H	80.4	1.472	1.484	1.473	1.498	1.476	30
						79.6				1.498		
ClPh	ClPh	Cl	Cl	H	H	83.4	1.543	1.517	1.546	1.508	1.535	30
						80.2				1.527		
Ph	Ph	Cl	Cl	H	H	73.9	1.520	1.529	1.480	1.495	1.510	1
						78.8				1.505		
Ph	Ph	Br	Br	H	H	72.2	1.509	1.508	1.477	1.493	1.498	1
						78.4				1.510		
Ph	Ph	CH_3	CO_2H	H	H	83.6	1.548	1.490	1.505	1.513	1.514	31
						70.2				1.505		
Me_2NPh	H	CN	ClPh	H	H	42.1	1.580	1.567	1.531	1.495	1.559	32
ClPh	CN	H	Me_2NPh	H	H	21.3	1.580	1.531	1.567	1.488	1.559	32
BrPh	H	H	$-\underset{\underset{O}{\Vert}}{C}-N(Ph)-\underset{\underset{O}{\Vert}}{C}-$		H	25.4	1.517	1.506	1.440	1.504	1.488	33
Ph	H	Br	Br	Ph	H	48.2	1.515	1.518	1.515	1.487	1.516	This work
O_2NPh	H	Br	Br	O_2NPh	H	52.3	1.516	1.517	1.516	1.493	1.516	This work
O_2NPh	H	H	C(O)CH_3	H	H	1.5	1.513	1.474	1.488	1.501	1.492	34
Ph	┌	Ph	OMe	┐[c]	H	57.2	1.526	1.513	1.527	1.479	1.522	35
Ph	OMe	Ph	┌	┐	H	47.4	1.526	1.527	1.513	1.478	1.522	35
Ph	┌	BrPh	OMe	┐[d]	H	67.4	1.537	1.510	1.553	1.477	1.533	35
						69.7	1.531	1.521	1.519	1.468	1.524	
BrPh	OMe	Ph	┌	┐[d]	H	24.5	1.537	1.553	1.510	1.478	1.533	35
						24.7	1.531	1.519	1.521	1.523	1.524	

[a] The data in this table were generated by the program ORFFE,[6] using the atomic coordinates and cell constants as published or received. Geometric parameters and numbering scheme are found in Figure 7. No attempt has been made to associate errors with these values. [b] The average of the three cyclopropane ring bond lengths. [c] ┌┐ is a representation of –C(O)–C(Ph)=C(H)–, where the carbonyl carbon serves as R^N where N is the smaller number. [d] There were two independent molecules in the asymmetric unit in this crystal structure.

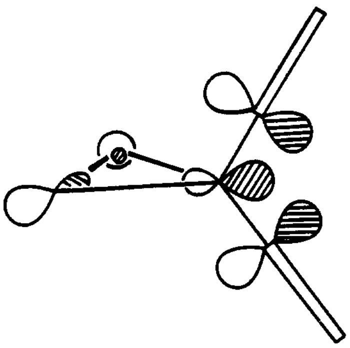


Figure 8. A representation of the orbital interaction involving a 4e′ cyclopropane orbital and *gem*-diphenyl substituents. The phenyl rings are in the perpendicular conformation.

or a special effect from *geminal* phenyl groups, is a prerequisite for the observation of such bond length changes.

The *p*-nitrophenyl-substituted cyclopropane, **2**, was prepared and characterized structurally in order to assess the sensitivity of the phenyl-cyclopropane interaction to changes in the electronic demand of the phenyl ring. We found that the cyclopropane ring is unaffected by the presence of the nitro groups. The phenyl-cyclopropane overlap (in either bisected or perpendicular conformations) does not improve (θ = 48° in **1** vs. 52° in **2**); the C(1)-C(4) bond (refer to the numbering scheme in Figure 7) does not shorten (1.487 (4) vs. 1.493 (4) Å); the average bond length of the cyclopropane ring remains the same (1.516 (5) vs. 1.516 (5) Å). Pertinent to the discussion of **2** is the structure of (*E*)-2-(4′nitrophenyl)cyclopropyl methyl ketone.[34] This structure displays the most nearly bisecting conformation (θ = 1.5°) and a short C(2)-C(3) bond length (1.49 (1) Å). The shortness of this bond, however, is tempered by the fact that the average bond length in this compound is 1.49 Å, and that the average bond lengths in ketone- or carboxylic acid-substituted cyclopropane rings are shorter than those of the parent compound. In addition, if a strong phenyl-cyclopropane interaction were present, the C(1)-C(4) bond length (1.50 (1) Å) should have been shorter than the equivalent bond lengths in compounds where there is little possible overlap. Since it is not, we take the θ value of 0° to be fortuitous.

A simple energetic argument can be advanced for the apparent preference for donation rather than acceptance of electron density by the benzene substituents. The energy difference between the 4e′ orbitals of cyclopropane and the $3e_{2g}$ (filled) orbitals of benzene is 14.5 eV. The energy difference between the 3e′ orbitals of cyclopropane and the $1e_{2u}$ (unfilled) orbitals of benzene is 18.1 eV.[38] Since the efficiency of orbital interaction increases with a decrease in orbital separation, the benzene-to-cyclopropane donation should be more favorable than the reverse. However, the need for more accurate calculations is acute.

From the structures of **1** and **2** it is evident that there is no large decrease in energy which accompanies the bisected or perpendicular conformations, as both **1** and **2** have the freedom to assume the necessary geometry. However, investigation of these structures has led to two useful conclusions: (1) bromine and probably chlorine substituents do not influence cyclopropane geometries extensively; and (2) the orbital interactions possible in the bisected conformation, so useful in predicting cyclopropylcarbinyl cation chemistry, play a far less active role in uncharged species, while the interactions possible in the perpendicular conformation may play an active role in stabilizing systems forced into that geometry.

It is clear that more work, both structural and theoretical, is needed to resolve the questions still surrounding the substituent–cyclopropane interaction. One attack is to compare structures of identical substitution where θ is fixed at 0 and 90°. Such studies are currently in progress.

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Supplementary Material Available: Tables II and V, which list the structure amplitudes for each structure (19 pages). Ordering information is given on any current masthead page.

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The Effects of Solvent–Solute Interactions on the Stereochemical Course of the High-Energy Chlorine-38 for Chlorine Substitution Process in Diastereomeric Dichloroalkanes in the Condensed Phase[1]

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Abstract: The stereochemistry of the high-energy chlorine-38 for chlorine substitution process was studied in diastereomeric 2,4-dichloropentane and 2,3-dichlorobutane in solutions. The experimental results indicate that the stereochemical course of the substitution process is predominantly and directly controlled by the properties of the solvent molecules, specifically by the dielectric constant, which in turn is responsible for the magnitude of intermolecular interaction between reactants and solvents. It appears that strong intermolecular interaction favors substitution via retention of configuration, whereas in solvents having a low dielectric constant the retention/inversion ratio decreases.

The role of solvents in determining the relative distribution and nature of reaction products in high-energy reactions, e.g., in photochemical or hot atom reactions, where the reactants are not in thermal equilibrium with the environment is still not completely understood and only relatively few studies have addressed themselves to this problem.[2-3] An especially instructive case for the evaluation of such solvent effects appears to be the investigation of those high-energy reactions which lead to substitution products either via retention or inversion of configuration, as, e.g., the ^{38}Cl for Cl substitution