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Structures of 1,1-Dichloro-2,2-diphenylcyclopropane and 1,1-Dibromo-2,2-diphenylcyclopropane. A Study of Substitution Effects on Cyclopropane Geometries

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Abstract: The structures of 1,1-dichloro-2,2-diphenylcyclopropane and 1,1-dibromo-2,2-diphenylcyclopropane have been determined from three-dimensional X-ray data collected by counter techniques. The compounds are isomorphous, crystallizing in the monoclinic space group C_{2h}^5-$P2_1/c$ with four molecules per cell. Cell constants for the chloro derivative are a = 6.170 (2), b = 13.673 (4), c = 15.513 (4) Å; and β = 92.24 (2)°; cell constants for the bromo compound are a = 6.246 (2), b = 13.822 (4), c = 15.640 (4) Å; and β = 93.88 (2)°. The structures have been refined by full-matrix least-squares procedures to conventional R indices of 0.034 (on F) and 0.046 (on F^2) for the chloro compound and 0.035 (on F) and 0.067 (on F^2) for the bromo derivative. Both structures have unsymmetrical cyclopropane rings with C–C bond lengths of 1.490 (3), 1.520 (3), and 1.529 (3) Å in the chloro compound and 1.477 (6) and 1.508 (6), and 1.509 (6) Å in the bromo compound. The longer bonds in the chloro compound may result from withdrawal of electrons from the cyclopropane ring as a whole. In each structure the shortest C–C bond is that across the ring from the point of phenyl substitution. For other cyclopropanes, this shortening has been observed previously across from substituents which can interact through π orbitals and has been explained by simple molecular orbital arguments. Such simple arguments do not explain the shortenings observed for the compounds studied here since the orientations of the phenyl rings do not allow overlap of the appropriate orbitals.

The unique ability of a cyclopropane ring to conjugate with neighboring π orbitals has long been recognized. Spectroscopic and chemical studies of various substituted cyclopropanes have shown that the cyclopropyl group is similar to a double bond in many respects.[1-4] It has been demonstrated that the cyclopropyl group is extremely effective at stabilizing carbonium ions.[1,2]

The molecular structures of numerous substituted cyclopropanes have been reported.[5-14] They show that substitution may cause major changes in the geometry of the cyclopropane ring. In order to assess more fully these effects, we have determined the crystal and molecular structures of 1,1-dichloro-2,2-diphenylcyclopropane and 1,1-dibromo-2,2-diphenylcyclopropane. Our findings are reported here along with comparisons with previously reported structural results.

Experimental Section

The compounds of 1,1-dichloro-2,2-diphenylcyclopropane and 1,1-dibromo-2,2-diphenylcyclopropane were prepared by standard literature methods.[15] Crystals suitable for X-ray work could be obtained from diethyl ether recrystallizations. Preliminary film work indicated that the compounds are isomorphous and crystallize in space group C_{2h}^5-$P2_1/c$.

Lattice parameters were obtained from a least-squares analysis of the setting angles of 16 reflections in the 2θ range 25–30° which had been centered on a FACS-I diffractometer using a takeoff angle of 1.1° and Mo Kα_1 radiation (λ 0.709030 Å) monochromatized from the (002) face of a highly mosaic graphite crystal.[16] The crystal data obtained for each compound are listed in Table I.

The intensity data were collected on the FACS-I diffractometer in shells of 2θ by the θ–2θ scan method using monochromatized Mo Kα radiation. Data collection methods have been detailed previously.[17] The details of the data collections are listed in Table I. During each data collection 6 standard reflections were monitored every 100 reflections and these showed only statistical variations.

The data were processed in the usual manner using a value of 0.04 for p.[16] The chloro compound yielded 2453 unique data which were used in F^2 refinements and 1525 reflections with $F_o^2 > 3\sigma(F_o^2)$, which were used in refinements based on F. The bromo derivative yielded 2396 unique data of which 1490 had $F_o^2 > 3\sigma(F_o^2)$.

The bromo structure was solved by symbolic addition using 299 rescaled values of $E < 1.60$.[18] The chloro derivative was refined first based on the solution found for the bromo compound. Once the refinement of the chloro structure was complete, refinement of the bromo derivative was begun using the final parameters of the chloro structure. Full-matrix least-squares techniques were employed,[17] and the details are listed in Table I. In both cases, the initial cycles of refinement were based on F, using only those reflections having $F_o^2 > 3\sigma(F_o^2)$. Because of the relatively large number of observations not satisfying this condition, final refinements were carried out on F_o^2, using all unique data, including those with $F_o^2 \leq 0$.

Tables II and III list the values of $100|F_o|$ and $100|F_c|$ (in electrons) for the chloro and bromo compounds, respectively.[19] These values are derived from the final cycle of F^2 refinement in each case. Those values of $|F_o|$ less than zero in the tables denote F_o^2 values observed to be less than zero. Tables IV and V list the values of the atomic parameters for the two structures. Table VI presents the root-mean-square amplitudes of vibration for each structure.

Results

The Crystal Structures. The two similar cyclopropane derivatives crystallize with nearly identical structures. Figure 1 presents a stereoview of the unit cell of the chloro derivative. The unit cell of the bromo compound is essentially the same. The packing is dominated by the phenyl rings. The closest intermolecular distances are in each case H–H contacts of about 2.35 Å.

The Molecular Structures. The molecular structures of the two cyclopropanes are similar. A view of the chloro de-

Table I. Crystal Data, Data Collection, and Refinement of the Structures

	Chloro	Bromo
Space group	$a = 6.170$ (2) Å	6.246 (2) Å
	$b = 13.673$ (4) Å	13.822 (4) Å
C_{2h}^5-$P2_1/c$, $Z = 4$	$c = 15.513$ (4) Å	15.640 (4) Å
	$\beta = 92.24$ (2)°	93.88 (2)°
Density (calcd)	1.297 g/cm³	1.735 g/cm³
Density (meas)	1.29 (1)	1.74 (1)
Data crystal	0.28 × 0.29 × 0.45 mm	0.18 × 0.24 × 0.55 mm
	Colorless prism	Colorless prism
Linear absorption coefficient (Mo Kα)	4.56 cm^{-1}	59.32 cm^{-1}
Transmission coefficients	0.94–0.96	0.24–0.40
	No correction made	Correction made
Data collection range (Mo Kα)	$3° \leq 2\theta \leq 51°$	$3° \leq 2\theta \leq 50°$
Data collected	$h, k \geq 0$	$h, k \geq 0$
Scan range and rate	1° below Mo Kα_1 to 1° above Mo Kα_2 at 1°/min	
Takeoff angle	2.3°	2.3°
Aperture, 32 cm from crystal	4.3 mm wide	3.7 mm wide
	5.5 mm high	4.0 mm high
Backgrounds	10 sec $2\theta \leq 26°$	40 sec $3° \leq 2\theta \leq 50°$
	20 sec $26° < 2\theta \leq 40°$	
	40 sec $2\theta > 40°$	
All atoms isotropic	$R^a = 0.14$	$R = 0.18$
refinement on F (for $F_o^2 > 3\sigma(F_o^2)$)	$R_w = 0.18$	$R_w = 0.21$
All anisotropic	$R = 0.073$	$R = 0.085$
	$R_w = 0.093$	$R_w = 0.098$
All anisotropic plus	$R = 0.034$	$R = 0.035$
isotropic H atoms on ring and phenyl H atoms with fixed positions	$R_w = 0.043$	$R_w = 0.039$
F^2 refinement as above with	$R(F^2)^b = 0.046$	$R(F^2) = 0.066$
all observations used	$R_w(F^2) = 0.099$	$R_w(F^2) = 0.089$
Final R indices (on F)	$R = 0.034$	$R = 0.035$
for $F_o^2 > 3\sigma(F_o^2)$	$R_w = 0.043$	$R_w = 0.038$
Standard deviation of observation of unit weight	1.193 electrons for 163 variables and 2453 data	1.162 electrons for 163 variables and 2396 data

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)^{1/2}$. [b] $R(F^2) = \Sigma|F_o^2 - F_c^2|/\Sigma F_o^2$ and $R_w(F^2) = (\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4)^{1/2}$.

Table IV. Positional and Thermal Parameters for the Atoms of 1,1-Dibromo-2,2-diphenylcyclopropane

Atom	x^a	y	z	β_{11}^b or B, Å²	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br (1)	−0.05629 (8)	0.26291 (4)	0.19073 (3)	26.80 (16)	7.54 (4)	4.85 (3)	−1.99 (6)	0.57 (5)	−0.97 (3)
Br (2)	0.01752 (8)	0.48726 (4)	0.17625 (3)	32.83 (18)	7.18 (4)	5.14 (3)	3.83 (6)	1.26 (5)	1.37 (3)
C1	0.1402 (7)	0.3672 (3)	0.21510 (26)	21.9 (13)	5.9 (3)	4.26 (21)	0.7 (5)	1.3 (4)	0.13 (20)
C2	0.2945 (6)	0.3640 (3)	0.29357 (26)	21.5 (13)	5.6 (3)	3.82 (19)	0.3 (5)	1.9 (4)	−0.15 (19)
C3	0.3706 (8)	0.3506 (4)	0.2049 (3)	27.4 (4)	6.6 (4)	4.28 (24)	0.8 (7)	2.1 (5)	0.07 (25)
C4	0.2929 (7)	0.2770 (3)	0.35190 (26)	26.8 (14)	4.37 (26)	3.81 (19)	−0.5 (5)	0.4 (4)	−0.21 (19)
C5	0.1232 (7)	0.2598 (3)	0.40277 (28)	34.0 (16)	5.8 (3)	4.18 (21)	−1.0 (6)	2.9 (5)	−0.22 (22)
C6	0.1306 (9)	0.1839 (4)	0.4603 (3)	46.1 (21)	6.8 (4)	4.11 (23)	−4.8 (6)	3.1 (6)	−0.63 (25)
C7	0.3095 (11)	0.1247 (4)	0.4675 (3)	57.4 (26)	5.5 (3)	5.09 (27)	−1.4 (8)	−0.7 (7)	0.30 (26)
C8	0.4775 (10)	0.1409 (4)	0.4174 (4)	45.4 (22)	6.0 (4)	7.0 (3)	4.0 (7)	−0.1 (7)	0.50 (28)
C9	0.4712 (8)	0.2168 (3)	0.3590 (3)	32.3 (16)	5.5 (3)	5.88 (26)	1.4 (6)	0.8 (5)	0.40 (24)
C10	0.3495 (7)	0.4562 (3)	0.33975 (27)	25.7 (14)	4.90 (27)	3.98 (20)	−0.9 (5)	0.8 (4)	0.56 (20)
C11	0.2048 (8)	0.4983 (3)	0.3920 (3)	34.8 (16)	4.7 (3)	4.91 (23)	−0.9 (5)	2.4 (5)	−0.37 (21)
C12	0.2602 (10)	0.5818 (4)	0.4379 (3)	50.9 (22)	5.5 (3)	5.07 (26)	0.7 (7)	1.3 (6)	0.01 (24)
C13	0.4599 (11)	0.6219 (4)	0.4325 (4)	53.9 (26)	5.3 (3)	6.3 (3)	−2.1 (8)	−5.0 (7)	0.45 (27)
C14	0.6019 (9)	0.5808 (4)	0.3811 (4)	33.4 (18)	7.0 (4)	8.8 (4)	−3.1 (7)	−2.6 (7)	1.0 (3)
C15	0.5482 (8)	0.4978 (4)	0.3351 (3)	29.2 (16)	6.1 (3)	6.69 (29)	−1.5 (6)	1.0 (5)	0.38 (25)
H1C3	0.404 (8)	0.295 (4)	0.189 (3)	3.3 (13)					
H2C3	0.445 (7)	0.401 (3)	0.1819 (25)	1.4 (10)					
H1C5	−0.001	0.299	0.397	5.5					
H1C6	0.006	0.172	0.494	6.2					
H1C7	0.318	0.074	0.510	7.4					
H1C8	0.600	0.098	0.422	7.0					
H1C9	0.589	0.227	0.324	6.0					
H1C11	0.062	0.472	0.396	5.6					
H1C12	0.158	0.612	0.474	6.7					
H1C13	0.495	0.680	0.463	7.0					
H1C14	0.743	0.611	0.378	6.8					
H1C15	0.653	0.467	0.302	6.2					

[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: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. The quantities given in the table are the thermal coefficients × 10³.

Table V. Postitional and Thermal Parameters for the Atoms of 1,1-Dichloro-2,2-Diphenylcyclopropane

Atom	x^a	y	z	β_{11},[b] or B, A^2	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cl (1)	−0.04009 (11)	0.27331 (5)	0.19031 (4)	30.19 (21)	10.01 (6)	4.94 (3)	−2.36 (8)	−0.58 (6)	−1.01 (3)
Cl (2)	0.02899 (11)	0.48178 (5)	0.17871 (4)	35.26 (23)	9.38 (6)	5.37 (3)	4.75 (9)	0.86 (7)	1.86 (3)
C1	0.1422 (4)	0.36943 (17)	0.21167 (14)	24.8 (7)	7.17 (17)	3.72 (10)	1.40 (28)	0.64 (21)	0.06 (11)
C2	0.2959 (3)	0.36554 (16)	0.29056 (13)	20.1 (6)	6.06 (15)	3.55 (9)	0.94 (24)	1.55 (19)	0.14 (10)
C3	0.3777 (4)	0.35275 (22)	0.19944 (16)	25.3 (8)	7.29 (19)	4.17 (11)	1.7 (3)	2.27 (22)	−0.25 (12)
C4	0.2919 (3)	0.27662 (16)	0.34765 (14)	25.8 (7)	4.93 (13)	3.64 (9)	−0.23 (25)	0.13 (20)	−0.63 (9)
C5	0.1163 (4)	0.25814 (17)	0.39877 (15)	32.2 (8)	5.95 (15)	4.05 (11)	−1.18 (28)	1.20 (23)	−0.20 (11)
C6	0.1204 (5)	0.18029 (20)	0.45596 (16)	46.1 (11)	6.86 (18)	4.15 (12)	−3.8 (4)	1.74 (28)	−0.24 (12)
C7	0.2998 (6)	0.11996 (19)	0.46179 (18)	60.0 (5)	5.64 (17)	4.82 (13)	−1.3 (4)	−2.6 (3)	0.37 (12)
C8	0.4730 (5)	0.13665 (20)	0.41091 (19)	46.5 (12)	6.63 (19)	6.45 (16)	3.7 (4)	−2.4 (3)	0.19 (14)
C9	0.4700 (4)	0.21472 (18)	0.35370 (17)	31.9 (8)	6.20 (16)	5.32 (12)	2.1 (3)	0.35 (25)	−0.19 (12)
C10	0.3489 (3)	0.45836 (16)	0.33776 (13)	23.9 (7)	5.11 (13)	3.64 (10)	0.68 (25)	0.52 (20)	0.61 (9)
C11	0.1986 (4)	0.50184 (18)	0.38995 (16)	34.9 (9)	5.94 (16)	5.05 (12)	−0.1 (3)	2.96 (26)	−0.10 (11)
C12	0.2506 (5)	0.58489 (20)	0.43695 (17)	50.5 (12)	5.84 (16)	5.04 (13)	0.8 (4)	2.9 (3)	−0.23 (12)
C13	0.4553 (6)	0.62545 (19)	0.43327 (18)	54.5 (13)	5.28 (17)	5.75 (14)	−1.0 (4)	−4.1 (3)	0.28 (13)
C14	0.6042 (5)	0.58354 (21)	0.38188 (21)	33.2 (9)	6.91 (19)	8.53 (19)	−3.3 (4)	−1.9 (3)	0.02 (16)
C15	0.5528 (4)	0.50021 (19)	0.33406 (18)	26.4 (8)	6.75 (18)	6.56 (14)	−0.4 (3)	0.61 (26)	0.40 (13)
H1C3	0.454 (4)	0.4078 (17)	0.1781 (15)	2.5 (6)					
H2C3	0.421 (4)	0.2895 (17)	0.1849 (14)	2.0 (5)					
H1C5	−0.010	0.300	0.394	5.4					
H1C6	−0.003	0.169	0.492	6.4					
H1C7	0.304	0.065	0.502	6.8					
H1C8	0.596	0.093	0.415	6.8					
H1C9	0.594	0.227	0.317	5.7					
H1C11	0.054	0.474	0.392	5.7					
H1C12	0.143	0.613	0.474	6.4					
H1C13	0.490	0.684	0.466	6.9					
H1C14	0.747	0.612	0.379	6.9					
H1C15	0.660	0.470	0.297	6.0					

[a] The thermal coefficients have been multiplied by 10^3.

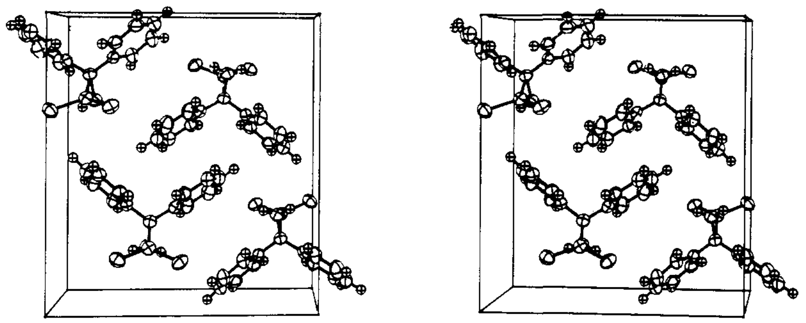


Figure 1. Stereoscopic view of the unit cell of 1,1-dichloro-2,2-diphenylcyclopropane. The y axis is horizontal, the z axis is vertical, and the x axis points out of the paper. The shapes of the atoms in this and the following drawings represent 50% probability contours of thermal motion. The phenyl H atoms are of arbitrary size.

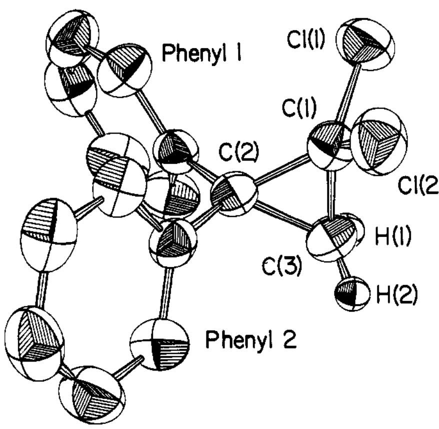


Figure 2. Perspective view of 1,1-dichloro-2,2-diphenylcyclopropane. Ring 1 contains C atoms C(4) through C(9) with C(4) bound to C(2). Ring 2 contains C atoms C(10) through C(15).

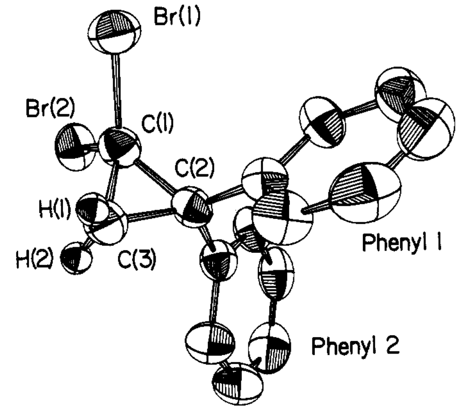


Figure 3. Perspective view of 1,1-dibromo-2,2-diphenylcyclopropane.

rivative is shown in Figure 2 and a different view of the bromo derivative in Figure 3. The labeling schemes are shown in the figures and are analogous for the two molecules. Figure 4 shows important intramolecular bond lengths and angles for both molecules. A complete list of bond lengths and angles can be found in Tables VII and VIII.

The phenyl groups are as far apart as possible as required

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

Atom	X = Cl Min	X = Cl Int	X = Cl Max	X = Br Min	X = Br Int	X = Br Max
X(1)	0.2225 (8)	0.2539 (8)	0.3154 (9)	0.2183 (7)	0.2401 (7)	0.2835 (7)
X(2)	0.2206 (9)	0.2551 (9)	0.3291 (9)	0.2142 (7)	0.2489 (7)	0.2991 (7)
C(1)	0.211 (3)	0.216 (3)	0.264 (3)	0.203 (7)	0.229 (6)	0.242 (6)
C(2)	0.185 (3)	0.215 (3)	0.242 (3)	0.192 (7)	0.226 (6)	0.233 (6)
C(3)	0.196 (3)	0.241 (3)	0.267 (3)	0.214 (7)	0.242 (6)	0.256 (7)
C(4)	0.196 (3)	0.224 (3)	0.229 (3)	0.203 (6)	0.219 (6)	0.231 (6)
C(5)	0.219 (4)	0.231 (3)	0.257 (3)	0.214 (6)	0.234 (6)	0.269 (6)
C(6)	0.223 (3)	0.238 (3)	0.312 (3)	0.217 (6)	0.232 (7)	0.323 (7)
C(7)	0.226 (4)	0.238 (3)	0.348 (4)	0.228 (7)	0.249 (7)	0.341 (8)
C(8)	0.230 (4)	0.274 (4)	0.323 (4)	0.221 (7)	0.294 (7)	0.314 (8)
C(9)	0.225 (3)	0.253 (3)	0.265 (3)	0.222 (7)	0.257 (6)	0.271 (6)
C(10)	0.198 (3)	0.213 (3)	0.233 (3)	0.201 (6)	0.225 (6)	0.236 (6)
C(11)	0.227 (3)	0.237 (3)	0.276 (3)	0.211 (7)	0.236 (6)	0.271 (6)
C(12)	0.230 (3)	0.245 (3)	0.316 (4)	0.231 (7)	0.250 (7)	0.317 (7)
C(13)	0.223 (4)	0.244 (3)	0.342 (4)	0.222 (7)	0.245 (7)	0.360 (8)
C(14)	0.222 (4)	0.277 (4)	0.329 (4)	0.229 (7)	0.265 (7)	0.349 (8)
C(15)	0.225 (3)	0.251 (3)	0.285 (3)	0.226 (7)	0.254 (6)	0.289 (6)

Table VII. Intramolecular Bond Distances (Å)

	X = Cl		X = Br	
C(1)–C(2)	1.520 (3)	1.525 (6)[a]	1.509 (6)	1.508 (6)
C(2)–C(3)	1.529 (3)		1.508 (6)	
C(3)–C(1)	1.490 (3)		1.477 (6)	
C(1)–X(1)	1.753 (2)	1.754 (2)	1.915 (4)	1.912 (4)
C(1)–X(2)	1.755 (2)		1.910 (4)	
C(2)–C(4)	1.505 (3)	1.500 (7)	1.510 (6)	1.502 (8)
C(2)–C(10)	1.495 (3)		1.493 (6)	
C(3)–H(1)	0.95 (2)	0.94 (2)	0.84 (5)	0.88 (5)
C(3)–H(2)	0.94 (2)		0.92 (4)	
C(4)–C(5)	1.391 (3)	1.383 (8)	1.388 (6)	1.381 (9)
C(5)–C(6)	1.385 (3)		1.380 (6)	
C(6)–C(7)	1.381 (4)		1.383 (7)	
C(7)–C(8)	1.373 (4)		1.370 (8)	
C(8)–C(9)	1.389 (4)		1.391 (7)	
C(9)–C(4)	1.387 (3)		1.388 (6)	
C(10)–C(11)	1.388 (3)		1.387 (6)	
C(11)–C(12)	1.381 (4)		1.391 (6)	
C(12)–C(13)	1.383 (4)		1.373 (8)	
C(13)–C(14)	1.366 (4)		1.361 (8)	
C(14)–C(15)	1.390 (4)		1.385 (7)	
C(15)–C(10)	1.385 (3)		1.374 (6)	

[a] Average value of equivalent bonds. Deviation given is the standard deviation of an individual distance based on averaging or of an individual measurement, whichever is larger.

Table VIII. Intramolecular Bond Angles (deg)

Angle	X = Cl		X = Br	
C(1)–C(2)–C(3)	58.5 (1)	60	58.6 (3)	60
C(2)–C(3)–C(1)	60.4 (1)		60.7 (3)	
C(3)–C(1)–C(2)	61.1 (1)		60.7 (3)	
X(1)–C(1)–X(2)	110.9 (1)		110.7 (2)	
X(1)–C(1)–C(2)	120.1 (2)	119.9 (3)	120.3 (3)	120.3 (3)
X(2)–C(1)–C(2)	119.6 (2)		120.3 (3)	
X(1)–C(1)–C(3)	118.9 (2)	118.6 (4)	118.5 (3)	118.4 (3)
X(2)–C(1)–C(3)	118.4 (2)		118.3 (3)	
C(4)–C(2)–C(1)	118.6 (2)	118.7 (2)	119.0 (4)	118.9 (4)
C(10)–C(2)–C(1)	118.8 (2)		118.8 (4)	
C(4)–C(2)–C(3)	117.7 (2)	118.0 (5)	118.3 (4)	118.3 (4)
C(10)–C(2)–C(3)	118.4 (2)		118.2 (4)	
C(4)–C(2)–C(10)	113.9 (2)		113.5 (3)	
H(1)–C(3)–C(1)	115 (1)	116 (1)	116 (4)	116 (4)
H(2)–C(3)–C(1)	118 (1)		116 (3)	
H(1)–C(3)–C(2)	114 (1)	115 (1)	118 (3)	118 (3)
H(2)–C(3)–C(2)	116 (1)		116 (3)	
H(1)–C(3)–H(2)	120 (2)		116 (4)	
C(5)–C(4)–C(2)	120.9 (2)	120.6 (5)	121.3 (4)	120.4 (9)
C(9)–C(4)–C(2)	120.1 (2)		119.1 (4)	
C(11)–C(10)–C(2)	120.7 (2)		120.4 (4)	
C(15)–C(10)–C(2)	120.8 (2)		120.7 (4)	
C(4)–C(5)–C(6)	120.6 (2)	120.0 (2)	120.7 (5)	120.0 (4)
C(5)–C(6)–C(7)	119.7 (2)		119.6 (5)	
C(6)–C(7)–C(8)	120.2 (2)		120.2 (5)	
C(7)–C(8)–C(9)	120.3 (3)		120.7 (5)	
C(8)–C(9)–C(4)	120.2 (2)		119.4 (5)	
C(9)–C(4)–C(5)	118.9 (2)		119.4 (4)	
C(10)–C(11)–C(12)	120.9 (2)		120.2 (5)	
C(11)–C(12)–C(13)	120.1 (2)		119.9 (5)	
C(12)–C(13)–C(14)	119.5 (2)		119.9 (5)	
C(13)–C(14)–C(15)	120.7 (2)		120.6 (5)	
C(14)–C(15)–C(10)	120.3 (2)		120.5 (5)	
C(15)–C(10)–C(11)	118.4 (2)		118.9 (4)	
Dihedral and Vector–Plane Angles				
C(1)–C(2)–C(3)— C(4)–C(6)–C(8)	126.1 (2)		126.8 (3)	
C(1)–C(2)–C(3)— C(10)–C(12)–C(14)	55.1 (2)		55.7 (3)	
C(4)–C(6)–C(8)— C(10)–C(12)–C(14)	71.1 (2)		71.4 (4)	
C(1)–C(3)— C(4)–C(6)–C(8)	78.7 (2)		78.6 (3)	
C(1)–C(3)— C(10)–C(12)–C(14)	105.9 (2)		107.8 (3)	

by their steric bulk. They are roughly parallel to the C(1)-C(3) bond across the cyclopropyl ring. The dihedral angles between the phenyl rings and the cyclopropane rings are listed in Table VIII. The phenyl rings are planar, with no atom deviating more than 0.01 Å from the best least-squares plane. The average C-C bond length found for the phenyl rings is 1.383 (8) and 1.381 (9) Å, respectively, for the chloro and bromo compounds. The C(4)-C(2) and C(10)-C(2) bond lengths average 1.502 (6) Å in the bromo derivative and 1.500 (5) (Å) in the chloro compound. In 6,6-diphenyl-3,3-diethyl-3-azabicyclo[3.1.0]hexane bromide, the corresponding distance averages 1.503 Å.[12] The C(4)-C(2)-C(10) bond angle is 113.5 (3)° in the bromo derivative, 113.9 (2)° in the chloro derivative, and 113° in the bicyclo compound.

The three-membered rings are unsymmetrical with unequal C-C bond lengths. The C(1)-C(3) bond length in the chloro derivative is 1.490 (3) Å, while the bonds adjacent to the phenyl substituents are longer, C(1)-C(2) is 1.520 (3) Å, and C(2)-C(3) is 1.529 (3) Å. All bonds in the bromo ring are shorter, but the same trend persists. The C(1)-C(3) bond is the shortest, 1.477 (6) Å, while C(1)-C(2) and C(2)-C(3) are longer and identical [1.509 (6) and 1.508 (6) Å]. The bond angles within the three-membered ring are thus fixed, with the smallest angle at atom C(2). The C(1)-C(2)-C(3) angle is 58.1 (1)° for the chloro compound and 58.6 (3)° for the bromo.

Table IX. A Comparison of Bond Lengths (Å) within Substituted Cyclopropane Rings

Compd	Substituents[a]	Adjacent bonds[b]	Cross ring bond[c]	Ref
Cyclopropane	H, H	1.5096 (15) 1.5096 (15)	1.5096 (15)	5
Chlorocyclopropane	Cl, H	1.514 (2) 1.514 (2)	1.514 (2)	6
1,1-Dichlorocyclopropane	Cl, Cl	1.532 (2) 1.532 (2)	1.532 (2)	7
Cyclopropanecarboxamide	$CONH_2$, H	1.502 (7) 1.512 (7)	1.481 (7)	8
Cyclopropanedicarboxylic acid	CO_2H, CO_2H	1.531 (3) 1.538 (3)	1.462 (4)	9
Cyclopropanecarbohydrazide	$CONHNH_2$, H	1.520 (15) 1.493 (15)	1.478 (15)	10
1-Chloro-1-phenylsulfonyl-2,3-dimethylcyclopropane	$SO_2C_6H_5$, Cl	1.508 (5) 1.512 (5)	1.499 (5)	11
N-Phenyl-2-(*p*-bromophenyl)-cyclopropane-1,3-dicarboximide	C_6H_5Br, H	1.516 (16)	1.439 (19)	12
2,5-Dimethyl-7,7-dicyano-norcaradiene	CN, CN	1.554 (3) 1.559 (3)	1.501 (5)	13
6,6-Diphenyl-3,3-diethyl-3-azabicyclo[3.1.0]hexane bromide	C_6H_5, C_6H_5	1.521 (4) 1.514 (4)	1.521 (5)	14
1,1-Dichloro-2,2-diphenyl-cyclopropane	C_6H_5, C_6H_5	1.520 (3) 1.529 (3)	1.490 (3)	*d*
1,1-Dibromo-2,2-diphenyl-cyclopropane	C_6H_5, C_6H_5	1.509 (6) 1.508 (6)	1.477 (6)	*d*

[a] The substituents on the carbon atom of the cyclopropane which has the most important substituent. [b] The lengths (Å) of he two bonds in the cyclopropane ring which are adjacent to the substituents. [c] The length of the bond across the cyclopropane ring from the substituent. [d] This work.

The Cl–C bond lengths average 1.754 (2) Å, which is slightly longer than in chlorocyclopropane or dichlorocyclopropane[6,7] (Table IX). The Cl–C–Cl bond angle is only 110.9 (1)°, nearly tetrahedral. The Br–C bond lengths average 1.912 (4) Å, and the Br–C–Br bond angle is 110.7 (2)°.

The hydrogen atoms of C(3) were found in difference Fourier maps and were refined. The H–C(3) bond lengths average 0.92 (4) Å, and the H–C–H bond angle is 120 (2)° in the chloro derivative and 116 (4)° in the bromo compound.

Discussion

The purpose of this study was to examine the effects of substituents on cyclopropane bond lengths. An examination of the bond lengths found within the three-membered rings of the molecules studied here demonstrates a dramatic difference between substituents which can interact through a π-orbital system, phenyls, and substituents which can only interact through σ orbitals, halogens.

Halogen Substituents. The effects of halogen substitution are evident. The halogen atoms primarily interact through σ bonds and are observed to have an effect on all bond lengths equally. The three ring C–C bonds in the chloro compound average 1.513 Å in length, which is longer than the average length of 1.498 Å in the bromo compound. The chlorine atoms with their greater electronegativity appear to withdraw electron density from the ring as a whole increasing all bond distances with respect to the bromo compound. The essential equality of equivalent distances in the two molecules, *e.g.*, the C–C bond distances within the phenyl rings, suggests that this effect is electronic and not the result of thermal motion.

The effect of halogen substitution has been observed before. As determined from experiments on the gases, cyclopropane, chlorocyclopropane, and 1,1-dichlorocyclopropane all have symmetrical structures within the precision of the measurements. The distances found are 1.510 (1) Å for cyclopropane, 1.514 (2) Å for chlorocyclopropane, and 1.532 (2) Å for 1,1-dichlorocyclopropane. Increasing substitution of chlorine atoms for hydrogen atoms lengthens all bond distances equally.

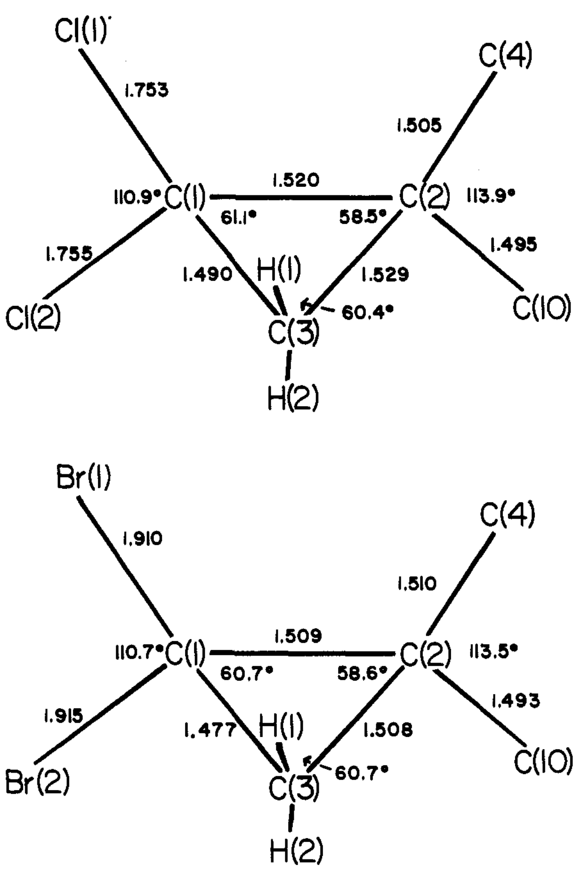


Figure 4. A representation of the two cyclopropanes showing important bond lengths (Å) and angles (deg).

The present chloro derivative has greater bond lengths in the cyclopropane ring than does the bromo derivative. The average bond length of the chloro compound is less, however, than that found in 1,1-dichlorocyclopropane. This may be a reflection of a σ-donating effect of the phenyl substituents, which supply electron density to the entire ring and thus shorten all bonds. It would obviously be useful to com-

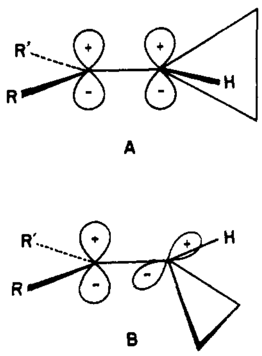
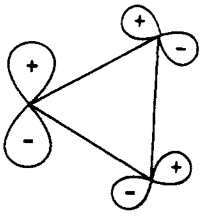


Figure 5. A representation of the two extreme geometries of a π-bonding substituent of a cyclopropane ring. In A, the molecule is in the "bisecting" orientation and there is overlap of the π orbitals. In B, the molecule is in the "perpendicular" orientation, and there is no overlap of the orbitals.

pare the molecular structure of 1,1-diphenylcyclopropane with these halogen derivatives and with cyclopropane itself.

Phenyl Substituents. The Walsh model for the bonding in cyclopropane provides useful insight into why the cyclopropyl group has its unique ability to conjugate with π-bonding substituents.[20] In the Walsh model, the highest occupied molecular orbital with the proper symmetry to interact with π substituents is 1. To interact or conjugate the substituent must have the proper orientation with respect to this orbital. The favorable orientation is that of parallel orbitals, the so-called "bisected" structure shown in Figure 5A. The π orbitals of the substituent are oriented correctly to interact with the Walsh orbital of the ring. This structure has been demonstrated for numerous cyclopropane derivatives[8,13] and for cyclopropane carbonium ions.[1,2]



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An examination of various known cyclopropane structures (Table IX) reveals that those with substituents which are not capable of π interactions have symmetrical ring structures in which all three C-C bond lengths are similar. Those which have substituents which can π-bond are not symmetrical. The bond across the ring from the point of substitution is distinctly shorter than the two bonds adjacent to the point of substitution. In all cases where this unsymmetrical ring is found, the π-interacting substituent has the "bisecting" orientation, and the appropriate π orbitals are parallel (Figure 5A).

These structural results are easily explained by the Walsh model. As shown by Hoffmann,[21] transfer of π-electron density out of the Walsh orbital 1 to a substituent will weaken the adjacent bonds for which this orbital has bonding character. The orbital has antibonding character for the bond across the ring from the point of substitution, and thus that bond is strengthened by a withdrawal of electron density from the orbital. The orbitals of the substituent can only overlap with the Walsh orbital if the molecule is in the "bisecting" orientation (Figure 5A).

Let us now consider the effect of a π substituent which is not in the favorable "bisecting" orientation. Spectroscopic and chemical studies have shown that phenylcyclopropane and 1,2-diphenylcyclopropanes are conjugated molecules, but that 1,1-diphenylcyclopropane is not.[3,4] The 1,1-diphenylcyclopropane molecule has two phenyl groups on one cyclopropane carbon atom, and their steric bulk forces them into an orientation such that the orbitals are not parallel but rather are perpendicular to one another. In this geometry, there is no possible overlap with the Walsh orbital, and thus no conjugation would be expected.

The molecular structure of 6,6-diphenyl-3,3-diethyl-3-azabicyclo[3.1.0]hexane bromide is consistent with this model.[14] As expected, the cyclopropane ring is symmetrical with equal C-C bond lengths within the ring. The phenyl rings are oriented such that there is no overlap of the appropriate orbitals. However, this compound is a quaternary ammonium salt and a bicyclic system, and thus the structural results may not be representative of all such cyclopropanes.

The structures reported here are also of 1,1-diphenyl-substituted cyclopropanes. Surprisingly they do not have symmetrical ring structures even though the phenyl groups are oriented such that the orbitals of the phenyl rings are nearly perpendicular to the π orbital of the cyclopropane ring. This angle between these orbitals is essentially equivalent to the angle the C(1)-C(3) vector makes with the normal to a phenyl ring. These vector-plane angles are 78.6 (2) and 105.9 (2)° in the chloro compound and 78.6 (2) and 107.8 (2)° in the bromo derivative. Since these angles are not precisely 90°, a slight overlap with the Walsh orbital is possible, but it seems unlikely that this overlap would result in the highly unsymmetrical rings that are observed.

An examination of the data presented in Table IX indicates that, although the differences in bond lengths between adjacent and cross ring bonds are not as great as in the extreme cases, they are real and of a magnitude comparable with most of the previously observed cases where the favorable "bisecting" orientation is found.

The shortening of the bond across the ring might be attributable to a steric effect of the phenyl rings, but this is unlikely since the geometry of the diphenyl portion of the molecule is very similar in the bicyclo system where a symmetrical structure was found.[14] Moreover, since the C(1)-C(2) and C(2)-C(3) bonds are equal within a given structure, there is no evidence of any severe steric interactions with the halogens.

We thus believe that the evidence presented here for unsymmetrical rings in 1,1-dichloro-2,2-diphenylcyclopropane and 1,1-dibromo-2,2-diphenylcyclopropanes is inconsistent with the simple, and previously unchallenged, molecular orbital picture for cyclopropanes.

Acknowledgment. This research was sponsored by the National Science Foundation through the Northwestern University Materials Research Center.

Supplementary Material Available. Tables II and III which list the structure amplitudes for each structure will appear following these papers in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche, referring to code number JACS-75-561.

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Reactions of Aromatic Radical Anions. XI. Kinetic Studies of the Reaction of Sodium Naphthalene and Anthracene with *n*-Hexyl Bromide and Chloride[1]

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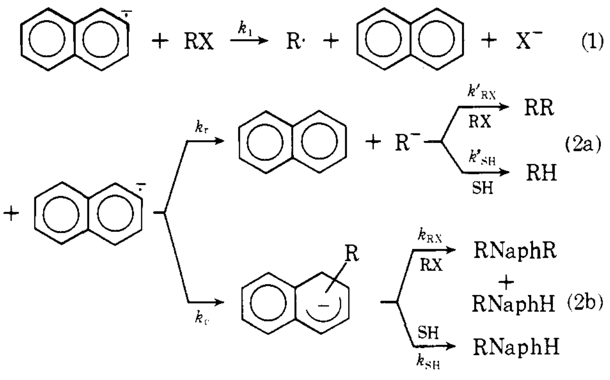
Received April 5, 1974

Abstract: The kinetics were studied for the irreversible electron-transfer reaction of sodium naphthalene and anthracene with *n*-hexyl bromide and chloride. The overall second-order dependence, with first-order dependency on the aromatic anion and the halide, supports the generally accepted mechanism. The hexyldihydronaphthyl anion, however, formed from alkyl radical–radical anion coupling, is a discrete intermediate and reacts surprisingly slowly with alkyl halide. The effect of halide variation on reaction rates indicates an unusual degree of selectivity, covering a range of 11 powers of 10. The effects are similar but smaller for chromium(II) or sodium atom reduction, suggesting that the aromatic provides a special, low-energy path for electron transfer. By varying the aromatic moiety, a linear relationship was found between the half-wave potentials and the rate constants, and an extrathermodynamic relationship is considered. Ion-pairing studies reveal that the reaction is faster for loose ion pairs than for tight ion pairs. Thus although a hard localized anion is formed in the reaction, the ion-pairing effects more closely resemble those of reversible electron transfer than those of the proton-abstraction reaction. Our interpretation of the irreversible electron transfer is that it involves an early transition state with little bond breaking and charge localization on the halide.

Aromatic radical anions, although long known as reactive species, have only recently been investigated in detail. Kinetic studies of proton abstraction and reversible electron-transfer reactions have contributed to the understanding of the mechanisms and the role of solvent and counter ions in these reactions.[2-10] Of particular importance has been the elucidation of the effects of ion pairing on the kinetics of aromatic radical anion reactions.

The description of the mechanism for the irreversible electron transfer with alkyl halides has, with notable exceptions, relied primarily upon product studies.[11-15] Bockrath and Dorfman report the rates of reactions of sodium biphenyl and sodium naphthalene with alkyl iodides and bromides utilizing pulse radiolysis techniques.[16] Previously, the scope of the reactions that had been examined was confined to slow reactions utilizing conventional rate studies.[17,18]

The mechanism proposed for the reaction of sodium naphthalene with alkyl halides involves the sequence of steps 1, 2a,b. As noted previously,[11b] the important slow step involving radical anion is the initial electron transfer to the alkyl halide yielding the alkyl radical (eq 1). Since reduction (k_r) and coupling (k_c) involve the radical, for a series of halides with identical alkyl groups, the rate constants for alkyl anion and alkyl dihydronaphthyl anion formation are the same (eq 2a,b). Also the reaction of alkyl anion and alkyl dihydronaphthyl anion with solvent is independent of the halide.



We have studied the aspects of the mechanism that are dependent upon the nature of the halide. These include the rate dependence upon halide variation for the decay of radical anion and the intermediacy of the alkyl dihydronaphthyl anion. In addition the results of studies on the effect of ion pairing on reactivity and the role of various radical anions and their reactivity with alkyl halides is considered.

Results and Discussion

The Rate Law. In the mechanism outlined above, the radical anion participates in two reaction steps, the transfer of an electron to the alkyl halide and subsequent reduction of the alkyl radical and the coupling of the alkyl radical with