kinson's catalyst in benzene-d_6. The solution was treated with hydrogen while it was stirred, and after 2 h the NMR spectrum of the solution indicated complete reduction. The solvent was removed, and the product was dissolved in pentane. It was passed through a small amount of nonactivated basic alumina. Removal of the solvent followed by sublimation gave pure **10**.

Silver Complex. A sample 21.2 mg (0.13 mmol) of recrystallized diene **1** was dissolved in 3 mL of pentane and was treated with a solution of 45.5 mg (0.27 mmol) of silver nitrate in 1 mL of water with vigorous stirring. The pentane and water were removed by freeze drying giving 58.5 mg of a gray powder. The ^{1}H NMR spectrum in D_2O solution (250 MHz, DSS ref) had bands at δ 2.71 (bd, J = 8 Hz) and 3.08 (bd, J = 8 Hz), and the ^{13}C spectrum had bands at δ 3.64 and 128.1. A pure sample was obtained by triturating the solid with methanol and removing the methanol from the solution under reduced pressure. Anal. Calcd for $C_{12}H_{16}(AgNO_3)_2$ Ag: 43.2%. Found: 44.2%.

In another experiment, 48 mg of **1** (0.30 mmol) was dissolved in 7 mL of pentane, and a solution of 105 mg (0.62 mmol) of silver nitrate in 2.5 mL of water was added dropwise with stirring. A white precipitate was formed. It was separated and washed with pentane (48 mg). Anal. Calcd for $C_{12}H_{16}AgNO_3Ag$: 32.7%. Found: 31.8%. The 1:1 adduct was insoluble in water but was soluble in aqueous silver nitrate solution giving the 2:1 adduct as shown by its NMR spectrum. The aqueous solution was freeze dried giving a gray powder, which was a mixture of the bis silver adduct and silver nitrate.

Acknowledgment. This investigation was supported by the National Science Foundation (Grant CHE-81-2421). Paul Okarma and Michael Matturro thank the Arthur Wayland Dox Foundation for fellowships.

Structure, Bonding, and Intramolecular Interactions in Tricyclo[4.2.2.2^{2,5}]dodeca-1,5-diene and Related Compounds

Kenneth B. Wiberg,* Richard D. Adams,* Paul J. Okarma, Michael G. Matturro, and Brigitte Segmuller

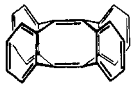
Contribution from the Department of Chemistry, Yale University, New Haven, Connecticut 06511. *Received October 26, 1983*

Abstract: The structure of tricyclo[4.2.2.2^{2,5}]dodeca-1,5-diene (**1**) has been determined by X-ray crystallography. The nature of the interaction between the double bonds of **1** was examined by comparing the observed geometry with that calculated by an ab initio procedure and by molecular mechanics. The effect of distortion on electron densities was examined by calculation using the wave function for **1**. Similar effects on other strained alkenes were examined. The effect of converting the double bonds to three-membered rings was examined via the crystallographic study of the diepoxide formed by the reaction of **1** with oxygen. The distortion produced by cross-ring bridging was examined by a crystallographic study of the dibromide formed from **1**, as well as by molecular mechanics calculations.

The double bonds of tricyclo[4.2.2.2^{2,5}]dodeca-1,5-diene (**1**)[1] are constrained to interact through space, and there may also be important through-bond interactions. In investigating these interactions, it is important to know accurately the distance between the double bonds.[2] This was determined by an X-ray crystallographic analysis.

An ORTEP diagram of the molecular structure of **1** is shown in Figure 1. The molecule is crystallographically centrosymmetrical and consists of two olefinic groups linked by four bridging $-CH_2CH_2-$ groups. Final positional and thermal parameters from the structural analysis are listed in Table I. Interatomic distances and angles are listed in Table II. The double bond, C_1-C_2, at 1.354 (1) Å is slightly longer than a normal double bond (e.g., C=C in C_2H_4 = 1.33 Å)[3] but compares very favorably with the C=C length, 1.35 Å, found in the related molecule 9,9,10,10-tetradehydrodianthracene (**2**).[4] The lengths of the four sp^3–sp^2 C–C single bonds, C_1-C_3, C_1-C_5, C_2-C_4, and C_2-C_6, are all very similar and range from 1.516 (1) to 1.521 (1) Å. However, the two independent sp^3–sp^3 C–C single bonds, C_3-C_4 and C_5-C_6, 1.595 (1) and 1.596 (1) Å, respectively are considerably longer than the normal value of 1.54 Å. All the hydrogen atoms were located and refined in the analysis. All C–H bond distances are normal and span the relatively narrow range 0.981–1.038 Å.

1



2

The intramolecular distance between the two double bonds in **1** is 2.395 (1) Å. The corresponding distance in **2** is 2.42 Å. Both of these distances are about 1.0 Å less than the $\pi-\pi$ C$\cdots$C van der Waals contact of 3.4 Å found for simple aromatic compounds.[5] It can safely be assumed that at this distance the interaction lies far into the repulsive region of the potential function. We have estimated that the strain energy of **1** is 44 kcal/mol.[1] The inherent strain in **1** appears primarily in the form of two molecular distortions: (1) the elongation of the C–C single bonds in the bridging CH_2CH_2 groups and (2) the nonplanarity of the double bonds

---

(1) Wiberg, K. B.; Matturro, M.; Adams, R. *J. Am. Chem. Soc.* **1981**, *103*, 1600. Wiberg, K. B.; Matturro, M.; Okarma, P. *Ibid.*, preceding paper in this issue.

(2) Honneger, E.; Heilbronner, E.; Wiberg, K. B. *J. Electron Spectrosc. Relat. Phenom.* **1983**, *31*, 369.

(3) Duncan, J. L.; Wright, I. J.; Van Lerberghe, D. *J. Mol. Spectrosc.* **1972**, *42*, 463.

(4) Viavattene, R. L.; Greene, F. D.; Cheung, L. D.; Majeste, R.; Trefonas, L. M. *J. Am. Chem. Soc.* **1974**, *96*, 4342.

(5) Pauling, L. "The Nature of the Chemical Bond"; Cornell University Press: Ithaca, NY, 1960; p 262.

Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations for Diene 1[a]

atom	*x*	*y*	*z*	*B*(1,1)	*B*(2,2)	*B*(3,3)	*B*(1,2)	*B*(1,3)	*B*(2,3)	*B*(equiv)
C1	0.58545 (8)	0.3428 (2)	0.52692 (8)	2.52 (2)	2.41 (4)	3.27 (2)	0.50 (3)	1.82 (1)	0.62 (3)	2.90 (2)
C2	0.55061 (8)	0.3493 (2)	0.59526 (8)	2.52 (2)	2.39 (4)	2.85 (2)	0.29 (3)	1.59 (1)	0.67 (3)	2.83 (2)
C3	0.48612 (9)	0.2720 (2)	0.38502 (9)	3.93 (2)	2.86 (4)	3.58 (2)	−0.05 (3)	2.66 (1)	−0.22 (3)	3.42 (3)
C4	0.60466 (8)	0.5230 (2)	0.69628 (8)	3.07 (2)	3.64 (5)	2.64 (2)	−0.15 (3)	1.69 (1)	0.12 (3)	3.38 (3)
C5	0.67903 (8)	0.5092 (2)	0.54981 (8)	2.52 (2)	3.97 (5)	4.00 (3)	0.14 (3)	2.19 (1)	0.66 (3)	3.56 (3)
C6	0.41123 (8)	0.2852 (2)	0.53141 (8)	3.17 (2)	2.90 (4)	3.79 (2)	−0.40 (3)	2.45 (1)	0.26 (3)	3.26 (2)

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
H3A	0.4301 (9)	0.151 (2)	0.3663 (9)	4.1 (3)	H5A	0.7181 (8)	0.456 (2)	0.5157 (9)	4.6 (3)
H3B	0.5341 (9)	0.227 (2)	0.3578 (9)	4.6 (3)	H5B	0.7526 (9)	0.550 (2)	0.6404 (9)	3.8 (3)
H4A	0.6976 (9)	0.559 (2)	0.7499 (9)	4.7 (3)	H6A	0.4101 (9)	0.250 (2)	0.6021 (9)	4.0 (3)
H4B	0.5978 (9)	0.479 (2)	0.7589 (9)	4.4 (3)	H6B	0.3764 (9)	0.161 (2)	0.4731 (9)	3.8 (3)

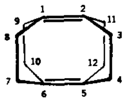
[a] The form of the anisotropic thermal parameter is $\exp[-\frac{1}{4}[h^2a^{*2}B(1,1) + k^2b^{*2}B(2,2) + l^2c^{*2}B(3,3) + 2hka^*b^*B(1,2) + 2hla^*c^*B(1,3) + 2klb^*c^*B(2,3)]]$.

Table II. Interatomic Distances (Å) and Angles (deg) with Estimated Standard Deviations for Diene 1[a]

atoms		atoms	
	Distances		
C_1–C_2	1.354 (1)	C_3–H_{3a}	0.981 (9)
C_1–C_3	1.517 (1)	C_3–H_{3b}	1.016 (9)
C_1–C_5	1.516 (1)	C_4–H_{4a}	0.970 (12)
C_2–C_4	1.517 (1)	C_4–H_{4b}	0.995 (9)
C_2–C_6	1.521 (1)	C_5–H_{5a}	1.004 (9)
C_3–C_4'	1.595 (1)	C_5–H_{5b}	0.970 (11)
C_5–C_6'	1.596 (1)	C_6–H_{6a}	1.038 (9)
C_1···C_2'	2.395 (1)	C_6–H_{6b}	0.983 (9)
	Angles		
C_2–C_1–C_3	120.65 (6)	C_1–C_5–H_{5a}	110.1 (5)
C_2–C_1–C_5	120.59 (7)	C_1–C_5–H_{5b}	115.1 (5)
C_3–C_1–C_5	109.96 (6)	C_2–C_6–H_{6a}	110.4 (5)
C_1–C_2–C_4	120.63 (6)	C_2–C_6–H_{6b}	113.0 (5)
C_1–C_2–C_6	120.65 (7)	C_4'–C_3–H_{3a}	109.8 (5)
C_4–C_2–C_6	110.06 (6)	C_4'–C_3–H_{3b}	110.3 (6)
C_1–C_3–C_4'	105.26 (6)	C_3'–C_4–H_{4a}	109.8 (5)
C_1–C_5–C_6'	105.40 (6)	C_3'–C_4–H_{4b}	110.2 (6)
C_2–C_4–C_3'	105.31 (6)	C_6'–C_5–H_{5a}	109.8 (6)
C_2–C_6–C_5'	105.10 (6)	C_6'–C_5–H_{5b}	109.1 (5)
C_1–C_3–H_{3a}	114.0 (6)	C_5'–C_6–H_{6a}	109.6 (5)
C_1–C_3–H_{3b}	110.4 (5)	C_5'–C_6–H_{6b}	110.1 (5)
C_2–C_4–H_{4a}	115.2 (6)	H_{3a}–C_3–H_{3b}	107.2 (7)
C_2–C_4–H_{4b}	110.9 (5)	H_{4a}–C_4–H_{4b}	105.4 (8)
		H_{5a}–C_5–C_{5b}	107.3 (7)
		H_{6a}–C_6–C_{6b}	108.5 (7)

[a] The numbering corresponds to that in Figure 1.

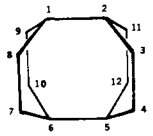
Table III. Comparison of Experimental and Calculated Geometries of Tricyclo[4.2.2.2^{2,4}|dodeca-1,5-diene (1)



			molecular mechanics		
parameter	exptl	ab initio	Boyd	MM2	Ermer
$r_{C=C}$	1.354	1.328	1.334	1.359	1.354
$r_{C_2C_3}$	1.517	1.535	1.518	1.526	1.537
$r_{C_3C_4}$	1.595	1.589	1.564	1.556	1.560
$d_{C_1C_6}$	2.395	2.399	2.324	2.351	2.430
$\angle C_1C_2C_3$	120.6	120.6	121.4	120.7	120.8
$\angle C_2C_3C_4$	105.3	105.3	104.4	105.1	106.4
$\angle C_3C_2C_{11}$	110.0	110.0	108.7	112.4	108.5
$\angle C_1C_2C_3C_{11}$ [a]	27.3	27.4	26.7	27.1	29.0

[a] Angle between the C_1–C_2 vector and the C_3–C_2–C_{11} plane.

Table IV. Geometry of Tricyclo[4.2.2.2^{2,5}]dodecane



		molecular mechanics	
parameter	ab initio	Boyd	MM2
$r_{C_1C_2}$	1.583	1.569	1.557
$r_{C_2C_3}$	1.553	1.547	1.542
$r_{C_3C_4}$	1.555	1.537	1.545
r_{C_1H}	1.089	1.093	1.120
r_{C_3H}	1.084 1.087	1.089 1.092	1.113 1.117
$d_{C_2C_5}$	2.805	2.773	2.740
$\angle C_1C_2C_3$	115.0	115.8	116.5
$\angle C_2C_3C_4$	113.8	113.4	113.0
$\angle C_8C_1C_9$	108.5	107.9	107.2
$\angle C_2C_1H$	105.5	105.4	105.1
$\angle C_8C_1H$	106.0	105.5	105.1
$\angle C_2C_3H$	107.6 110.0	108.2 111.1	108.1 112.2
$\angle HC_3H$	105.9	105.0	103.4

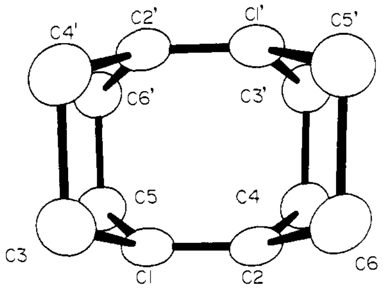


Figure 1. Perspective ORTEP diagram of $C_{12}H_{16}$ (**1**) showing 50% probability thermal motion ellipsoids.

and their substituents. The nature of the latter is apparent in the following ways: (1) the olefinic carbon atoms C_1 and C_2 lie 0.40 Å out of the plane defined by the atoms C_3, C_4, C_5, and C_6; (2) the dihedral angle between the plane of the substitutents and each of the planes defined by C_1, C_3, C_5 and C_2, C_4, C_6 are 27.3°; (3) the dihedral angle between the planes C_1, C_2, C_3, C_6 and C_1, C_2, C_4, C_5 is 35.6°. These dihedral angles would be 0.0° in a planar alkene. The C–C–C interatomic angles of the methylene groups range from 105.1° to 105.4°. These values appear to be a compromise between the ideal value of 109.5° for a tetrahedral carbon atom and 90°, which would be imposed on these angles if the double bonds were planar. All other angles appear to be normal. The shortest intermolecular distances are normal van der Waals contacts between hydrogen atoms at 2.5 Å. A packing diagram of **1** is shown in Figure 2.

The nature of the interaction between the double bonds, and the consequences thereof, has been of interest to us. To help understand this interaction, we have calculated the geometry of **1** via an ab initio geometry optimization using the STO-3G basis

Table V. Positional and Thermal Parameters and Their Estimated Standard Deviations for Diepoxide 4[a]

atom	x	y	z	$B(1,1)$	$B(2,2)$	$B(3,3)$	$B(1,2)$	$B(1,3)$	$B(2,3)$
O	0.1467 (1)	0.1783 (1)	0.1110 (1)	3.97 (4)	3.58 (4)	3.24 (4)	−1.27 (4)	−0.52 (4)	−0.67 (4)
C1	0.1122 (2)	0.1019 (2)	−0.0006 (1)	2.82 (5)	2.77 (5)	2.65 (5)	−0.63 (5)	−0.29 (5)	−0.12 (5)
C2	0.0430 (2)	0.1814 (2)	−0.1048 (2)	4.63 (7)	3.37 (6)	3.32 (6)	−0.83 (6)	−0.47 (6)	0.97 (6)
C3	0.0491 (2)	−0.0700 (2)	0.1747 (2)	4.21 (6)	4.55 (7)	2.52 (5)	−0.90 (7)	−0.71 (6)	0.83 (6)
C4	0.0326 (2)	0.0741 (2)	0.1107 (1)	3.12 (5)	3.05 (5)	2.38 (5)	−0.62 (5)	−0.19 (5)	−0.57 (5)
C5	−0.1174 (2)	0.1255 (2)	0.1193 (2)	3.74 (6)	3.95 (6)	4.09 (7)	0.08 (6)	0.84 (6)	−1.17 (6)
C6	0.2092 (2)	−0.0147 (2)	−0.0479 (2)	2.54 (5)	4.40 (7)	3.80 (6)	−0.04 (6)	0.44 (6)	−0.35 (6)
H1	0.112 (2)	0.218 (2)	−0.158 (2)	4.0					
H2	−0.019 (2)	0.259 (2)	−0.075 (2)	4.0					
H3	0.149 (2)	−0.102 (2)	0.173 (2)	4.0					
H4	0.016 (2)	−0.060 (2)	0.259 (2)	4.0					
H5	−0.130 (2)	0.223 (2)	0.080 (2)	4.0					
H6	−0.144 (2)	0.128 (2)	0.208 (1)	4.0					
H7	0.260 (2)	−0.062 (2)	0.019 (1)	4.0					
H8	0.276 (2)	0.026 (2)	−0.101 (2)	4.0					

[a] The form of the anisotropic thermal parameter is $\exp[-\frac{1}{4}[h^2a^{*2}B(1,1) + k^2b^{*2}B(2,2) + l^2c^{*2}B(3,3) + 2hka^*b^*B(1,2) + 2hla^*c^*B(1,3) + 2klb^*c^*B(2,3)]]$.

Table VI. Interatomic Distances (Å) and Angles (deg) with Estimated Standard Deviations for Epoxide 4[a]

atoms		atoms	
	Distance		
$O-C_1$	1.457 (1)	C_2-H_1	0.947 (8)
$O-C_4$	1.458 (1)	C_2-H_2	0.998 (8)
C_1-C_2	1.516 (1)	C_3-H_3	1.004 (8)
C_1-C_4	1.467 (1)	C_3-H_4	0.985 (9)
C_1-C_6	1.516 (1)	C_5-H_5	1.003 (8)
C_2-C_3'	1.561 (1)	C_5-H_6	1.008 (7)
C_3-C_4	1.516 (1)	C_6-H_7	0.986 (8)
C_4-C_5	1.517 (1)	C_6-H_8	0.945 (8)
C_5-C_6'	1.563 (1)	$C_1\cdots C_4'$	2.459 (1)
	Angles		
$O-C_1-C_4$	59.83 (4)	$C_1-C_2-H_1$	110.1 (4)
$O-C_1-C_2$	120.09 (6)	$C_1-C_2-H_2$	111.5 (5)
$O-C_1-C_6$	119.82 (6)	$C_3'-C_2-H_1$	108.8 (5)
$C_2-C_1-C_6$	110.75 (6)	$C_3'-C_2-H_2$	107.5 (4)
$C_2-C_1-C_4$	119.33 (6)	$C_4-C_3-H_3$	110.9 (5)
$C_4-C_1-C_6$	118.74 (6)	$C_4-C_3-H_4$	108.8 (5)
C_1-O-C_4	60.43 (4)	$C_2'-C_3-H_3$	109.6 (5)
$O-C_4-C_1$	59.74 (4)	$C_2'-C_3-H_4$	110.0 (5)
$O-C_4-C_3$	120.17 (6)	$C_4-C_5-H_5$	111.6 (4)
$O-C_4-C_5$	120.13 (6)	$C_4-C_5-H_6$	107.9 (4)
$C_1-C_4-C_3$	119.22 (6)	$C_6'-C_5-H_5$	107.9 (4)
$C_1-C_4-C_5$	119.32 (6)	$C_6'-C_5-H_6$	111.2 (4)
$C_3-C_4-C_5$	110.27 (7)	$C_1-C_6-H_7$	111.2 (5)
$C_1-C_2-C_3'$	107.42 (6)	$C_1-C_6-H_8$	109.8 (5)
$C_1-C_6-C_5'$	107.17 (6)	$C_5'-C_6-H_7$	111.2 (5)
$C_4-C_3-C_2'$	107.03 (6)	$C_5'-C_6-H_8$	109.8 (5)
$C_4-C_5-C_6'$	107.20 (6)	$H_1-C_2-H_2$	111.4 (6)
		$H_3-C_3-H_4$	110.6 (6)
		$H_5-C_5-H_6$	111.0 (6)
		$H_7-C_6-H_8$	107.6 (7)

[a] The numbering corresponds to that in Figure 7.

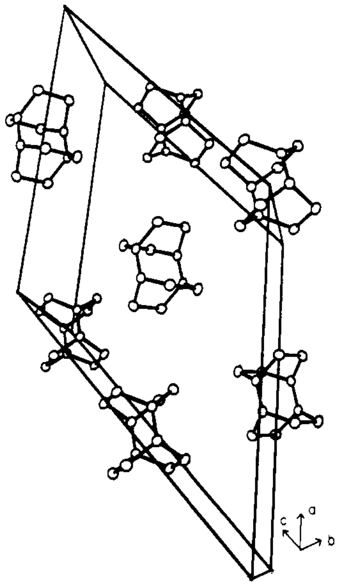


Figure 2. Crystal packing diagram of $C_{12}H_{16}$ (**I**).

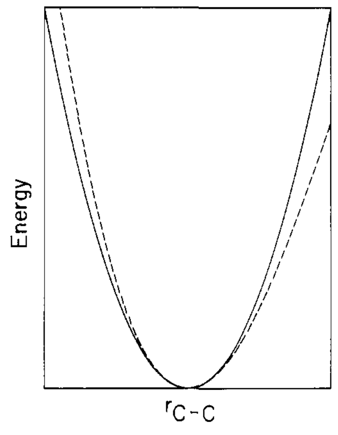


Figure 3. Harmonic (solid line) and anharmonic (dashed line) C–C bond stretching potentials.

set.[1] It was not possible to use a larger basis set with a molecule this size, but it is known that, although this basis set does not reproduce the difference in energy between alkanes and alkenes correctly, it generally gives reasonable geometries. The optimized geometry is compared with the X-ray result in Table III. It can be seen that the two most significant features of the X-ray structure, the distance between the double bonds and the long outside C–C bonds, are well reproduced.

It is not readily possible to analyze the wave functions to separate the various contributions to the intramolecular potential. However, some information might be obtained by comparing the calculated structure with those obtained via molecular mechanics. Several different force fields are in use with these calculations, and the results using the parameters of Boyd,[6] Allinger (MM2)[7], and Ermer[8] are compared with the ab initio and experimental geometries in Table III.

There are two apparent differences between the molecular mechanics results and the experimental (and ab initio) structure.

---

(6) Chang, S.-J.; McNally, D.; Shary-Tehrany, S.; Hickey, M. J.; Boyd, R. H. *J. Am. Chem. Soc.* **1970**, *92*, 3109.

(7) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127. Burkert, U.; Allinger, N. L. *ACS Mongr.* **1982**, *No. 177*.

(8) Ermer, O. "Aspekte von Kraftfeldrechnungen"; W. Baur Verlag: Munich, 1981.

Table VII. Positional and Thermal Parameters and Their Estimated Standard Deviations for $C_{12}H_{16}Br_2$ (6)[a]

atom	x	y	z	$B(1,1)$	$B(2,2)$	$B(3,3)$	$B(1,2)$	$B(1,3)$	$B(2,3)$
Br	0.3255 (1)	0.34132 (8)	0.15852 (9)	4.59 (2)	3.74 (2)	3.75 (2)	−2.04 (1)	−1.39 (1)	0.04 (2)
C1	0.0814 (8)	0.1996 (7)	0.3012 (7)	2.9 (1)	2.5 (2)	2.6 (1)	−0.5 (1)	−1.3 (1)	−0.6 (1)
C2	0.0706 (9)	0 1017 (8)	0.1544 (7)	4.1 (2)	3.3 (2)	2.2 (1)	−0.8 (1)	−1.7 (1)	−0.5 (1)
C3	−0.1726 (9)	0.3445 (8)	0.3969 (7)	3.8 (2)	2.3 (2)	3.1 (2)	−0.2 (1)	−1.7 (1)	−0.6 (1)
C4	0.1156 (7)	0.0241 (7)	0.4770 (7)	2.6 (1)	2.5 (1)	2.5 (1)	−0.5 (1)	−1.10 (9)	−0.9 (1)
C5	−0.0714 (8)	−0.0530 (8)	0.3103 (7)	4.0 (2)	3.2 (2)	2.6 (1)	−0.8 (1)	−1.9 (1)	−0.7 (1)
C6	−0.3137 (8)	0.1901 (8)	0.5536 (8)	2.4 (1)	2.8 (2)	3.3 (2)	0.0 (1)	−1.3 (1)	−0.7 (1)
H21	0.014 (10)	0.205 (9)	0.061 (9)	5.0 (2)					
H22	0.247 (8)	0.046 (8)	0.060 (7)	3.0 (1)					
H31	−0.218 (9)	0.447 (8)	0.285 (7)	4.0 (1)					
H32	−0.159 (9)	0.438 (8)	0.440 (8)	4.0 (1)					
H51	−0.231 (8)	−0.020 (8)	0.307 (7)	3.0 (1)					
H52	0.001 (9)	−0.196 (8)	0.300 (7)	4.0 (1)					
H61	−0.459 (8)	0.196 (7)	0.538 (7)	3.0 (1)					
H62	−0.409 (9)	0.206 (8)	0.702 (8)	4.0 (1)					

[a] The form of the anisotropic thermal parameter is $\exp[-\frac{1}{4}[h^2a^{*2}B(1,1) + k^2b^{*2}B(2,2) + l^2c^{*2}B(3,3) + 2hka^*b^*B(1,2) + 2hla^*c^*B(1,3) + 2klb^*c^*B(2,3)]]$.

Table VIII. Interatomic Distances (Å) and Angles (deg) with Estimated Standard Deviations for Dibromide 6[a]

atoms		atoms	
	Distance		
C_1–Br	1.963 (3)	C_2–H_{21}	0.91 (4)
C_1–C_2	1.550 (4)	C_2–H_{22}	1.03 (3)
C_1–C_3	1.535 (4)	C_3–H_{31}	0.98 (4)
C_1–C_4	1.502 (4)	C_3–H_{32}	0.91 (4)
C_2–C_5	1.570 (5)	C_5–H_{51}	0.99 (3)
C_3–C_6	1.567 (5)	C_5–H_{52}	0.97 (3)
C_4–C_4'	1.570 (6)	C_6–H_{61}	1.00 (3)
C_4–C_5'	1.555 (4)	C_6–H_{62}	1.01 (3)
C_4–C_6'	1.564 (4)		
	Angles		
Br–C_1–C_2	111.9 (2)	C_5–C_2–H_{21}	121 (3)
Br–C_1–C_3	112.5 (2)	C_5–C_2–H_{22}	120 (2)
Br–C_1–C_4	116.2 (2)	C_6–C_3–H_{31}	124 (2)
C_1–C_2–C_5	102.0 (2)	C_6–C_3–H_{32}	121 (2)
C_1–C_3–C_6	102.5 (2)	C_2–C_5–H_{51}	115 (2)
C_1–C_4–C_4'	93.4 (3)	C_2–C_5–H_{52}	116 (2)
C_1–C_4–C_5'	123.7 (2)	C_4'–C_5–H_{51}	107 (2)
C_1–C_4–C_6'	123.2 (2)	C_4'–C_5–H_{52}	110 (2)
C_2–C_1–C_3	107.3 (3)	C_3–C_6–H_{61}	118 (2)
C_2–C_1–C_4	104.0 (2)	C_3–C_6–H_{62}	120 (2)
C_2–C_5–C_4'	102.8 (2)	C_4'–C_6–H_{61}	110 (2)
C_3–C_1–C_4	104.0 (2)	C_4'–C_6–H_{62}	115 (2)
C_3–C_6–C_4'	102.4 (2)	H_{21}–C_2–H_{22}	100 (3)
C_4–C_4'–C_5	102.5 (3)	H_{31}–C_3–H_{32}	93 (3)
C_4–C_4'–C_6	101.5 (3)	H_{51}–C_5–H_{52}	107 (3)
C_5–C_4'–C_6	106.0 (2)	H_{61}–C_6–H_{62}	92 (3)
C_1–C_2–H_{21}	108 (2)		
C_1–C_2–H_{22}	105 (2)		
C_1–C_3–H_{31}	108 (2)		
C_1–C_3–H_{32}	108 (2)		

[a] The numbering corresponds to that in Figure 8.

First, none of the molecular mechanics calculations reproduced the lengthening of the outside C–C single bonds. The increased bond length may be due to through-bond coupling between the double bonds and the ethano bridges as has been suggested in the case of *p,p′*-dibenzene.[9] However, it is equally likely that the C–C stretching potential is anharmonic in the sense shown in Figure 3, whereas the molecular mechanics calculations use a harmonic function. Then, these calculations would overestimate the distortion energy for stretching a C–C bond at distances relatively far from equilibrium.[10] We have found considerable C–C bond elongation in other cases such as *trans*-bicyclo[4.1.0]heptane[11] and the dibromide **6**, which is considered below.

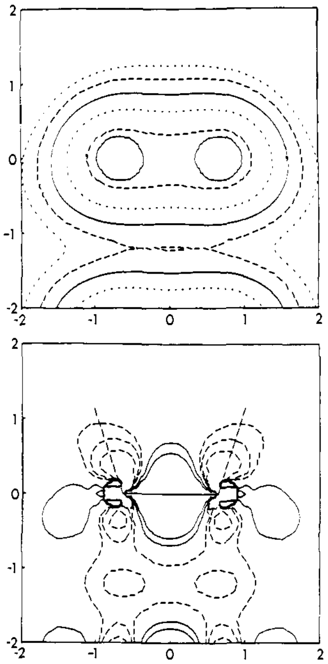


Figure 4. Electron density map for the diene **1** in the plane containing the two double bonds. The upper plot gives the electron densities (contours at 0.5, 0.25, 0.125, 0.063, 0.032, and 0.016 e/Bohr^3), and the lower plot gives the deformation densities (upper plot less the electron densities for four spherically averaged carbons at the appropriate locations, contours at 0.02, 0.01, 0.005 (solid), −0.02, −0.01, and −0.005 (dashed) e/Bohr^3).

Molecular mechanics does not reproduce these long bonds, and bond lengthening is not likely to be due to through-bond interactions in these cases.

Second, it may be noted that the parameters of Boyd and of Allinger led to too small a distance between the double bonds. However, decreasing the C–C stretching force constant for large extensions would lengthen the bridging C–C bonds and increase the distance between the double bonds to be in good accord with the measured value. On the other hand, Ermer's potential is too large, leading to a larger distance than observed. Since this is obtained even with shorter than observed bridging C–C bonds, it must be quite a bit too large. Correspondingly, Ermer's parameters lead to too large a calculated enthalpy of formation.

The pyramidalization at the double bonds of **1** must lead to some distortion of the electron density distribution. This may be examined in an electron density map obtained from the calculated

---

(9) Dougherty, D. A.; Schlegel, H. B.; Mislow, K. *Tetrahedron* **1978**, *34*, 1441.

(10) An anharmonic potential for both C–H and C–C bond stretching has recently been applied to molecular mechanics calculations: Lifon, S.; Stern, P. S. *J. Chem. Phys.* **1982**, *77*, 4542.

(11) Wiberg, K. B.; Lupton, E. C., Jr.; Wasserman, D. J.; de Meijere, A.; Kass, S. R. *J. Am. Chem. Soc.* **1984**, *106*, 1740.

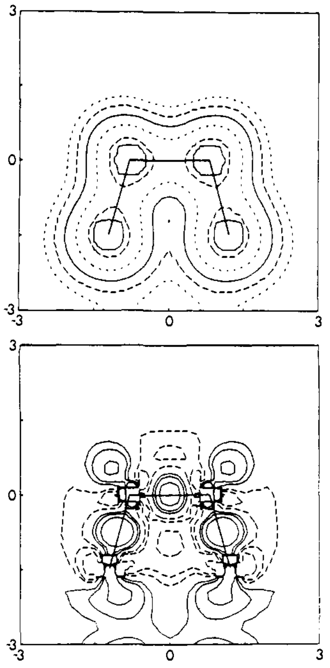


Figure 5. Electron density map for the diene **1** in the plane containing the $=CCH_2CH_2C=$ group. The contours are as in Figure 4.

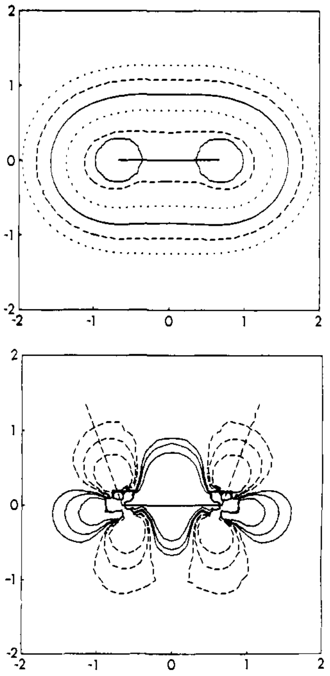


Figure 6. Electron density map for bicyclo[1.1.0]butene. The upper plot gives the electron densities in the symmetry plane containing the double bond, and the lower plot gives the deformation densities. The contours are as in Figure 4.

wave functions. The split valence 4-31G basis set should give a good representation of the electron density distribution, and the wave function obtained using this basis set has been employed in the following calculations.[1]

The densities in the plane containing the two double bonds are shown in Figure 4, and those in the plane containing the $=CCH_2CH_2C=$ tetrad are shown in Figure 5. It is difficult to gain information from the electron densities themselves, and thus the deformation densities[12] (the difference between the calculated densities and the densities expected from just the atoms at the respective coordinates) are frequently more useful. They are also shown in the figures.

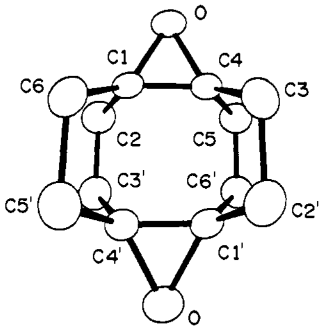


Figure 7. Perspective ORTEP diagram of $C_{12}H_{16}O_2$ (**4**) showing 50% probability thermal motion ellipsoids.

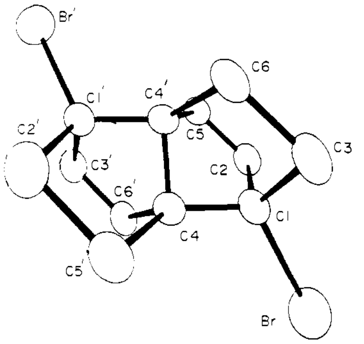
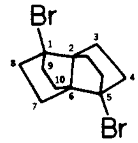


Figure 8. Perspective ORTEP diagram of $C_{12}H_{16}Br_2$ (**6**) showing 50% probability thermal motion ellipsoids.

Table IX. Comparison of Experimental and Calculated Geometries of 1,5-Dibromotetracyclo[4.2.2.2^{2,5}.0^{2,6}]dodecane



parameter	exptl	MM2
C_1-Br	1.963	1.945
C_1-C_2	1.502	1.531
C_1-C_8	1.535, 1.550	1.547
C_2-C_3	1.564, 1.555	1.546
C_2-C_6	1.570	1.549
C_3-C_4	1.567, 1.570	1.546
∡Br-C_1-C_8	112.2, 111.9	113.3
∡Br-C_1-C_2	116.2	114.2
∡C_1-C_2-C_3	123.2, 123.7	122.7
∡C_1-C_2-C_6	93.4	90.6
∡C_2-C_1-C_8	104.0	104.0
∡C_2-C_3-C_4	102.4, 102.8	101.7
∡C_3-C_4-C_5	102.5, 102.0	102.4
∡C_3-C_2-C_{12}	106.0	106.7
∡C_3-C_2-C_6	101.5, 102.5	104.3
∡C_8-C_1-C_9	107.3	107.1

We have calculated wave functions for other alkenes that are believed to be pyramidalized, such as bicyclo[1.1.0]butene, bicyclo[2.1.0]pentene, and bicyclo[3.1.0]hexene.[13] Electron density maps were calculated from the 6-31G* wave functions for bicyclobutene giving the results shown in Figure 6. A comparison of Figures 4 and 6 shows some qualitative similarities in the effect of pyramidalization at the double bond. Thus, the regions from which electron density is taken in order to form the double bonds

---

(12) Dunitz, J. "X-ray Analysis and the Structure of Organic Molecules"; Cornell University Press: Ithaca, NY, 1979; p 391ff.

(13) Wagner, H.-U.; Szeimies, G.; Chandrasekhar, J.; Schleyer, P. v. R.; Pople, J. A.; Binkley, J. S. *J. Am. Chem. Soc.* **1978**, *100*, 1210. Wiberg, K. B.; Bonneville, G.; Dempsey, R. *Isr. J. Chem.* **1982**, *23*, 85.

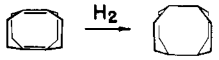
Table X. Crystallographic Data for X-ray Diffraction Studies

	Compound		
	1	4	6
formula	$C_{12}H_{16}$	$C_{12}H_{16}O_2$	$C_{12}H_{16}Br_2$
temp (±3 °C)	−25	25	25
space group	*C*2/*c*	*Pbca*	$P\bar{1}$
a, Å	13.942 (4)	9.580 (2)	6.609 (2)
b, Å	6.239 (2)	9.258 (2)	7.318 (1)
c, Å	14.198 (4)	11.012 (2)	7.485 (2)
α, deg			69.08 (2)
β, deg	133.91 (3)		62.24 (2)
γ, deg			64.72 (2)
V, Å^3	889.8 (10)	976.7 (6)	283.9 (1)
M_r	160.26	192.3	320.08
Z	4	4	1
ρ_{calcd}, g/cm^3	1.20	1.31	1.87
	Measurement of Intensity Data		
radiatn	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)
monochromator	graphite	graphite	graphite
detector aperture, mm			
horizontal ($A + B \tan \theta$)			
A	3.0	3.0	3.0
B	1.0	1.0	1.0
vertical	4.0	4.0	4.0
crystal faces	$20\bar{1}, \bar{2}01, 01\bar{1}$ $0\bar{1}1, 1\bar{1}\bar{1}, \bar{1}11$	$\bar{1}\bar{1}0, 110, \bar{1}10$ $1\bar{1}0, 102, \bar{1}0\bar{2}$	
crystal size, mm	0.4 × 0.5 × 0.5	0.5 × 0.7 × 0.4	0.4 × 0.5 × 0.5
crystal orientation direction, deg from 0 axis	*c**, 8.34	normal to 102, 8.6	
reflcns measured	$h, k, \pm l$	$+h+k+l$	$h \pm k \pm l$
max 2θ	60°	60°	60°
scan type	moving crystal, stationary counter	moving crystal, stationary counter	moving crystal, stationary counter
ω scan width: ($A + 0.347 \tan \phi$)°	1.05	0.80	0.90
bkgd	addnl scan at each end of scan	addnl scan at each end of scan	addnl scan at each end of scan
ω scan rate (variable)			
max, deg/min	10.0	10.0	10.0
min, deg/min	1.7	1.3	1.5
no. reflcns measured	1437	1649	1073
data used ($F^2 > 3.0\sigma(F^2)$)	921	932	890
	Treatment of Data		
absrpn coeff	0.62	0.81	75.2
P factor	0.02	0.02	0.02
final residuals			
R_F	0.040	0.043	0.042
R_{wF}	0.047	0.045	0.053
esd of unit weight obsd	2.67	4.72	3.37
largest shift/error value of final cycle	0.00	0.00	0.01
largest peak in final diff Fourier, e$^-$/Å^3	0.25	0.35	0.55

are canted outward in both cases. However, an examination of the bonding region shows a significant difference. In the case of bicyclobutene, the bonding density is clearly moved outward, whereas in the diene **1** it appears to have moved somewhat inward. The reason for this difference will receive further study.

The deformation density for the $=CCH_2CH_2C=$ group shown in Figure 5 shows that these bonds are relatively normal. Some bond bending is seen for the $=CCH_2$ C–C bond, but it is small compared to the degree of pyrimidalization at the double bond. It can be seen that the distortion at the double bonds of **1** does lead to significant rehybridization.

The repulsion between the carbons bearing the double bonds should be considerably reduced if the diene were reduced to the saturated hydrocarbon. Catalytic hydrogenation could be effected using Wilkinson's catalyst or diimide giving tricyclo[4.2.2.2^{2,5}]dodecane (**3**).[14] It is interesting to note that both double bonds



1 **3**

were readily reduced, whereas this catalyst normally is unreactive toward tetrasubstituted double bonds.[15] Although a solid, the crystals are waxy and easily deformed, and we have not as yet been able to obtain crystals suitable for X-ray crystallography. Nevertheless, the ab initio calculation reported in the preceding paper led to calculated geometry that should be reasonably good in view of the agreement between the observed and calculated structures for the diene **1**. The ab initio geometry is compared with the results of molecular mechanics calculations[16] by using Allinger's MM2 parameters as well as those of Boyd in Table IV. In general, Boyd's parameters gave the better fit to the ab initio geometry. The cross-ring distance has now increased to 2.8 Å,

---

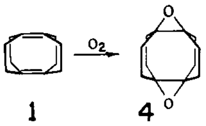
(14) This hydrocarbon has been prepared by other procedures: Eaton, P. E.; Chakraborty, U. R. *J. Am. Chem. Soc.* **1978**, *100*, 3634. Ernest, B.; Ganter, C. *Helv. Chim. Acta* **1978**, *61*, 1775.

(15) Crabtree, R. *Acc. Chem. Res.* **1979**, *12*, 331.

(16) Molecular mechanics calculations for **3** have been reported by: Osawa, E. *J. Am. Chem. Soc.* **1979**, *101*, 5523. The D_2 and D_{2h} conformations were calculated to differ in energy only 1 kcal/mol.

and the main component of the strain energy is the eclipsed geometry of the ethano bridges. The most interesting aspect of the geometry is the relatively long C_1–C_2 bond. It would have been interesting to know whether or not this is correct.

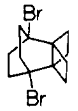
We next examined the effect of converting the double bonds into three-membered rings. The diene **1** reacts with oxygen to form a diepoxide, **4**. Details of the molecular structure of **4** were obtained experimentally by a single-crystal X-ray diffraction analysis. An ORTEP diagram of the structure of **4** is shown in Figure 7. Final positional and thermal parameters are listed in Table V. Interatomic distances and angles are listed in Table VI. As with **1**, **4** also contains a crystallographically imposed center of symmetry. The epoxide rings do not appear to contain any unusual distortions. The C–C and C–O distance in the ring at 1.467 (1), 1.457 (1), and 1.458 (1) Å are similar to those reported previously for epoxide rings contained in constrained carbocyclic rings.[17-19] The four external O–C–C angles, which lie within the range 119.82 (6)–120.17 (6)°, also appear to be normal. Thus, we believe that the epoxide groupings in **4** do not contain any significant stress caused by the other geometrical constraints in the molecule.



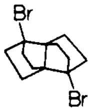
1 **4**

In addition, there appears to be a release in the strain on the bridging C–C single bonds on going from **1** to **4**. The C_2–C_3 and C_5–C_6 distances at 1.561 (1) and 1.563 (1) Å are a full 0.03 Å shorter than those in **1** and have approached closely the typical C–C sp^3–sp^3 single bond value of 1.54 Å. The C–C–C bond angles at the methylene groups in **4** have opened slightly (av 107.21 (9)°) compared to those in **1** (av 105.26 (6)°). As a result, the transannular distance between the carbon atoms of the epoxides at 2.459 (1) Å is larger than the corresponding distance in **1**, 2.395 Å. The hydrogen atoms in **4** were located and refined and show fairly normal bonding distances and angles. The shortest nonbonding intermolecular contacts were between hydrogen atoms at normal van der Waals distances, 2.50 (1) Å. The hydrogen atoms in **4** were located and refined and show fairly normal bonding distance and angles. The shortest nonbonding intermolecular contacts were between hydrogen atoms at normal van der Waals distances, 2.50 (1) Å.

The reaction of **1** with bromine leads to a dibromide.[20] It was not possible to distinguish betweent the two possible structures, **5** and **6**, on the basis of spectroscopic data. The correct formulation, **6**, was established by means of an X-ray crystallographic analysis.



5



6

An ORTEP diagram of the molecular structure of **6** is shown in Figure 8. Final positional and thermal parameters are listed in Table VII. Interatomic distances and angles are summarized in Table VIII. The molecule is crystallographically centrosymmetric and can be visualized as a combination of two bromine-substituted norbornane rings fused along a common 1,7-bond, C_4–$C_{4'}$. Except for the C_4–$C_{4'}$ bond, 1.570(5) Å, which is lengthened slightly, and the C_1–C_4 bond, 1.502 (4) Å, which is shortened slightly, all the C–C interatomic bonding distances are very similar to those in norbornane.[21] However, evidence for strain in the molecule was revealed by the large exterior bond angles C_1–C_4–$C_{5'}$ and C_1–C_4–$C_{6'}$ of 123.7 (2)° and 123.2 (2)°, respectively. This might induce a slight rehybridization of the bonding orbitals on C_4 in a way that could explain both the lengthening of the C_4–$C_{4'}$ bond and the shortening of the C_1–C_4 bond. For example, if a rehybridization in the direction of sp^2–p hybrids occurred, the "equatorial" bonds of C_4 to C_1, $C_{5'}$ and $C_{6'}$ would contain a greater degree of s character and might show contraction. At the same time the "axial" C_4–$C_{4'}$ bond would contain greater p character and would be lengthened. Except for the fact that C_4–$C_{5'}$ and C_4–$C_{6'}$ do not show any significant contraction, this is as observed. The shortest intramolecular nonbonded contacts in the crystal of **5** were between hydrogens at approximately 2.5 Å.

A comparison of the X-ray structure with that derived using the MM2 force field is shown in Table IX. The bond angles are generally in good agreement, but the bond lengths in the experimental structure again have a considerably larger range of values than that found in the molecular mechanics calculation. Thus, we again have reason to think that the bond stretching potential used in the latter is too stiff.

Experimental Section

Crystallographic Analyses. All diffraction measurements were made on an Enraf-Nonius CAD-4 fully automatic X-ray diffractometer. Crystals of the diene **1** were obtained by slow sublimation in a room maintained at 4 °C. A well-formed crystal was selected, mounted in a glass capillary at 4 °C, and transferred to the diffractometer equipped with an Enraf-Nonius Model FR524H low-temperature accessory precooled to −25 °C. Crystals of the diepoxide **4** and the dibromide **6** were obtained by slow crystallization from chloroform/ether and a chloroform, respectively. Crystal data and data collection parameters for all three structures are listed in Table X.

For **1**, the systematic absence *hkl*, $h + k = 2n + l$, and $h0l$, $1 = 2n + l$, are consistent with either of the two space groups *C*2/*c* or *Cc*. Structure solutions were attempted in both space groups and both yielded a reasonable preliminary structure. However, refinement in the noncentric space group converged very slowly and yielded a structure of much poorer quality, as judged by its molecular dimensions, than the structure obtained from the centric space group. The latter was thus deemed to be the correct one. The structure was solved by direct methods (MULTAN) using 124 reflections ($E > 1.41$). All programs were those of the Enraf-Nonius SDP library, and all calculations were carried out using a DEC PDP 11/45 computer. Atomic scattering factors were calculated by standard procedures.[22a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[22b] Full-matrix least-squares refinement minimized the function

$$\sum_{hkl} w(|F_{obsd}| - |F_{calcd}|)^2$$

where $w = 1/[\sigma(F)^2]$, $\sigma(F) = \sigma(F_{obsd}^2)/2F_{obsd}$ and $\sigma(F_{obsd}^2) = [\sigma(I_{raw})^2 + (PF^2_{obsd})^2]^{1/2}/(Lp)$.

Final positional and thermal parameters are given in Table I. Bond distances and angles with estimated standard deviations derived from the inverse matrix obtained in the final cycle of refinement are listed in Table II. A table of structure factor amplitudes is available (see supplementary material).

For **4**, the space group *Pbca* was established from the systematic absences observed during data collection. The structure was solved by direct methods (MULTAN) using 132 reflections with $E > 1.76$ and was refined as described above.

For **6**, the space group $P\bar{1}$ was assumed and confirmed by successful solution and refinement of the structure. This structure was solved by the heavy atom method and refined as described above. Tables of structure factor amplitudes for **4** and **6** have been published.[1,20]

Acknowledgment. This investigation was supported by N.S.F. Grant CHE-81-2421.

Registry No. 1, 77422-56-1.

Supplementary Material Available: Tables of structure factor amplitudes for 1 (4 pages). Ordering information is given on any current masthead page.

---

(17) Druck, U.; Luttke, W. *Acta Crystallogr., Sect. B* **1981**, *37B*, 1417.

(18) Kaftory, M. *Acta Crystallogr., Sect. B* **1980**, *36B*, 2668.

(19) Dunand, A.; Gerdil, R. *Acta Crystallogr. Sect. B* **1980**, *36B*, 472.

(20) Matturro, M. G.; Adams, R. D.; Wiberg, K. B. *J. Chem. Soc., Chem. Commun.* **1981**, 879.

(21) Chiang, J. F.; Wilcox, C. F., Jr.; Bauer, S. H. *J. Am. Chem. Soc.* **1968**, *90*, 3149.

(22) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1975; Vol. IV, (a) Table 2.2B, p 99–101, (b) Table 2.3.1, p 149–150.