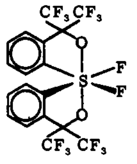
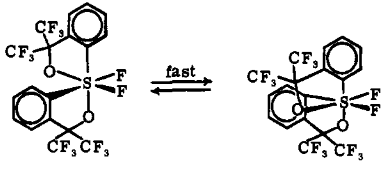
The ^{19}F NMR for **2a** shows two unresolved six-fluorine (CF_3) multiplets at −74.3 and −74.7 ppm and an unresolved multiplet at 77.0 ppm (2, S–F).[2] Structures **2a** and **2b** are compatible with the NMR data. If permutational isomerization of the all-cis structure **2c** [**2c**(c,c,c)], interconverting the enantiomers as shown, is fast on the NMR time scale, this could also be a possible structure. The choice of **2a** is based on a complete X-ray crystallographic structure to be reported later.

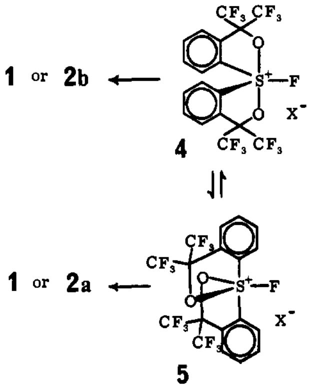


2b(c,c,t)



2c(c,c,c)

A reasonable route for the formation of **1** and **2** involves a common intermediate, trigonal-bipyramidal (TBP) persulfonium salt **4** (X = F). Attack of fluoride at the sulfur opposite fluorine leads to the kinetically preferred all-trans isomer (**1**), while attack at either of the other two positions in the equatorial plane gives the unobserved cis isomer (**2b**). Formation of the observed cis isomer (**2a**) could occur by pseudorotation of **4** to give the higher energy TBP conformer **5**, with equatorial oxygen and apical carbon, followed by attack of fluoride in the equatorial plane of **5** to provide either **1** or **2a**. We have reported the formation of **1** in the reaction of **4** (X = PF_6) with amines,[1] evidence for kinetically favored attack on **4** or **5** to give **1**.



Most, but not all, known compounds of hexacoordinate chalcogens (S, Se, Te) have all-trans geometries. Denney has reported[3] the low-temperature syntheses of some thermally unstable tetrafluoropersulfuranes, R_2SF_4, including a few which were constrained to a cis geometry by a ring system.[5] Cady reported[4] the only previous example of a *cis*-persulfurane, $SF_4(OSF_5)_2$, which was not thus constrained. There are no reported examples of the isolation of both cis and trans isomers of the same persulfurane. The only other chalcogen for which the isolation of cis and trans isomers of the same composition has been reported is tellurium.[5]

The permutational isomerization of **1** to **2** could be imagined to occur by a nondissociative mechanism. A twist mechanism[6] such as the Bailar twist[7] (a process maintaining C_3 symmetry) or the Ray and Dutt twist[8] (C_2 symmetry) involves no bond rupture. The lower limit for the activation energy for isomerization of **1** to **2** by such a twist process is >45 kcal/mol. This was determined by heating a solution of **1** in quinoline at 235 °C for 18 h, with no detectable formation of the more stable isomer **2a**.

Addition of a catalytic amount of SbF_5 to a CH_2Cl_2 solution of **1** results in rapid isomerization of **1** to **2**. None of the trans isomer has been detected by ^{19}F NMR.[9] Since SbF_5 is known to convert **1** or **2a** to persulfonium salt **4** (X = SbF_6), it is reasonable to assume that this rapid acid-catalyzed isomerization of **1** to **2** occurs by a dissociative mechanism. Persulfonium ion intermediate **4** (X = SbF_6) is detectable in the ^{19}F NMR of the isomerization mixture. The formation of **2a**, rather than **1**, in the oxidation of the sulfurane with excess BrF_3 is attributed to the Lewis acidity of BrF_3.

The greater thermodynamic stability of **2a** relative to **1** was further confirmed by calorimetry.[10] The difference in the heat of hydrolysis of the cis and trans isomers to the same sulfurane oxide (**3**) was found to be 2.0 ± 0.5 kcal/mol at 28 °C.[11]

The recently reported isomerizations of a series of hexacoordinated phosphorus anions (12-P-6 species) showed the cis isomers to predominate in equilibrium at room temperature.[12] A related thermodynamic preference for unsymmetrically apically substituted sulfurane (10-S-4) species has been noted.[13]

The greater stability of **2a** relative to **1** may reflect the ionic resonance energy in a unsymmetrically substituted three-center four-electron bond, an effect parallel to that long known to be important in two-center two-electron bonds.[13] The structure **2a** has two O–S–F three-center bonds, while **1** has one O–S–O and one F–S–F three-center bond. The present work leaves unanswered the question of the relative stabilities of the unobserved isomers **2b** and **2c**.

Acknowledgment. This research was supported in part by a grant from the National Science Foundation (Grant 7905692). We thank Michael R. Ross for the construction of the calorimeter which we used.

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(2) Fluorine chemical shifts are expressed in ppm downfield from $CFCl_3$.

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(9) Because of interference by overlapping peaks in ^1H and ^{19}F NMR spectra, it is difficult to identify unambiguously or to quantify the small amount of **1** in equilibrium with **2a**.

(10) We used a calorimeter built by Michael R. Ross in an adaptation of plans by Arnett et al. and Beak et al. [Arnett, E. M.; Bentrude, W. G.; Burke, J. J.; Duggleby, P. M. *J. Am. Chem. Soc.* **1965**, *87*, 1541. Beak, P.; Bonham, J.; Lee, J. T. *Ibid.* **1968**, *90*, 1569.]

(11) The value of ΔH for the hydrolysis of **1** in a solution of $PhCH_3/CF_3CO_2H$ (2:1 v/v) containing 1% H_2O was −12.4 kcal/mol and for the hydrolysis of **2a**, −10.4 kcal/mol.

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Synthesis, Structure, and Stability of (i,o)-Bicyclo[6.2.2]dodeca-9,11-dienes. Generation of Unusually Expanded Carbon–Carbon–Carbon Bond Angles

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Received September 8, 1980

The last two decades have witnessed extensive progress in our accumulation of knowledge of highly strained carbon–carbon bonds.[1] The vast majority of the studies which exist deal with

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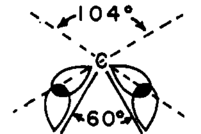
(1) For a recent review, see A. Greenberg and J. F. Liebman, "Strained Organic Molecules", Academic Press, New York, 1978.

relatively small strained rings in which we picture the interorbital angle as exceeding the internuclear angle in accord with the classical Coulson–Moffitt concept.[2] Indeed, physical measurements would appear to confirm that the contraction of a C–C–C internuclear angle, as in cyclopropane (**1**), results in major electron



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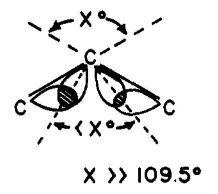
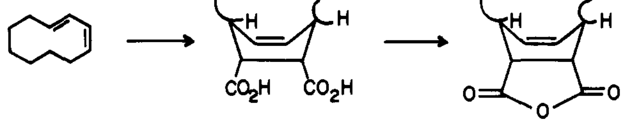


2

density existing outside the internuclear lines in so-called "bent" bonds or orbitals.[3] In contrast, relatively little is known[4] about the bonding or chemical properties of molecules having C–C–C internuclear angles far in excess of the normal tetrahedral angle of 109.5°. In principle, as the internuclear angle is expanded far beyond 109.5°, the interorbital angle should also be expanded but to a lesser extent. Thus, here again, the location of maximum bonding electron density should not coincide with the internuclear line as illustrated in **2**. We now wish to report the synthesis, single crystal X-ray structure determination, and some chemical properties of a molecule which possesses a saturated (sp^3-type) C–C–C bond angle of 124°.

In principle, the enlargement of a C–C–C bond angle can be best achieved via either steric repulsion as in di-*tert*-butylmethane,[4a–d] or stretching of the carbon chain as in polymers[4e] and [7]-paracyclophanes.[4f] We felt that a combination of these two effects could be used advantageously to produce large distortions of this type. Our previous experience with (i,o)-bicyclo[*n*.2.2]alkane derivatives[5] suggested that, in structures where *n* was sufficiently small, very large distortions of C–C–C bond angles might occur. To test this concept we have prepared the first derivatives of the (i,o)-bicyclo[6.2.2]dodecene system.

Treatment of *cis,trans*-cyclodeca-1,3-diene (**3**)[6] with maleic anhydride at 132 °C for 24 h followed by hydrolysis to the diacid



3 4 5

gave a 6% yield of **4**, mp 76–78 °C.[7] On exposure to dicyclohexylcarbodiimide, **4** was converted to the crystalline anhydride, **5**, in 76% yield; mp 75.0–76.5 °C; ^{1}H NMR (CDCl$_3$) δ 6.05 (2 H, m), 3.40 (2 H, m), 3.02 (2 H, m), 2.36–0.68 (12 H, m); ^{13}C NMR (CDCl$_3$) δ 175.1, 173.1, 136.2, 131.8, 48.4, 47.6, 39.1, 34.7, 31.9 (2 C), 30.7 (2 C), 29.4, 27.1.

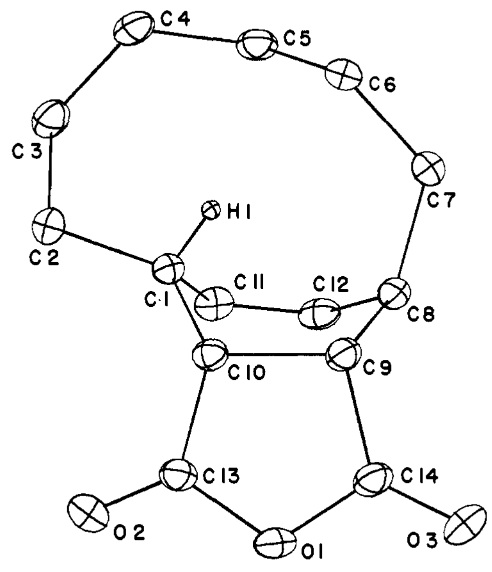


Figure 1. ORTEP drawing of **5** with all hydrogens except H-1 omitted for clarity.

Table I. Selected Bond Lengths and Bond Angles for **5**

bond	bond length, A	bond	bond length, A
C1–C2	1.520 (2)	C1–C10	1.535 (1)
C2–C3	1.533 (2)	C1–C11	1.500 (1)
C3–C4	1.548 (2)	C11–C12	1.317 (2)
C4–C5	1.549 (2)	C9–C14	1.511 (1)
C5–C6	1.549 (2)	C10–C13	1.502 (1)
C6–C7	1.536 (2)	C13–O2	1.192 (1)
C7–C8	1.567 (2)	C13–O1	1.387 (1)
C8–C9	1.563 (2)	C14–O3	1.186 (1)
C8–C12	1.507 (2)	C14–O1	1.381 (2)
C9–C10	1.537 (2)		

bonded atoms	bond angles, deg	bonded atoms	bond angles, deg
C1–C2–C3	107.76 (10)	C9–C8–C12	109.01 (09)
C2–C3–C4	116.25 (11)	C1–C11–C12	116.61 (10)
C3–C4–C5	118.44 (11)	C1–C10–C9	108.98 (09)
C4–C5–C6	117.19 (11)	C9–C10–C13	104.44 (09)
C5–C6–C7	118.73 (12)	C10–C9–C14	103.42 (09)
C6–C7–C8	123.88 (10)	C9–C14–O1	110.47 (10)
C8–C9–C10	114.89 (08)	C10–C13–O1	109.93 (09)
C8–C12–C11	118.95 (10)	C10–C1–C2	122.08 (09)
C7–C8–C9	115.09 (10)	C11–C1–C2	116.13 (10)
C7–C8–C12	114.68 (10)	C13–O1–C14	110.66 (09)

A single-crystal X-ray analysis of **5** was performed. The white crystals of $C_{14}H_{18}O_3$ belonged to the monoclinic space group $P2_1/c$. The measured cell constants, a = 14.868 (1) Å, b = 7.548 (1) Å, c = 10.824 (2) Å, β = 99.05 (1)°, gave a calculated density of 1.297 g/cm^3 for four molecules in the unit cell at ambient temperature. Data were collected on a fully-automated Enraf-Nonius CAD4 diffractometer by using a variable rate ω–2θ scan technique and graphite monochromatized Cu Kα radiation (λ = 1.54184 Å). After Lorentz-polarization corrections, 1616 of 2091 unique reflections (77%) with 2θ = 0–140° were observed for [$F_o \geq 2\sigma(F_o)$]. A combination of direct methods and difference Fourier synthesis was used to locate all nonhydrogen atoms.[8]

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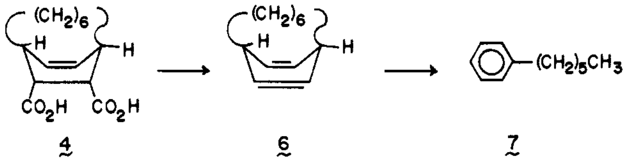
J. Am. Chem. Soc. **1981**, *103*, 217–219

Table II. Atomic Coordinates of All Atoms of **5**

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
O1	0.03852 (7)	0.1997 (2)	0.4133 (1)	H1	0.283 (1)	0.353 (2)	0.322 (2)
O2	0.14304 (8)	−0.0110 (2)	0.4961 (1)	H2A	0.342 (1)	0.070 (2)	0.304 (2)
O3	−0.03582 (7)	0.4425 (2)	0.3388 (1)	H2B	0.349 (1)	0.050 (2)	0.463 (2)
C1	0.27045 (9)	0.2676 (2)	0.3823 (1)	H3A	0.446 (1)	0.308 (2)	0.497 (1)
C2	0.34844 (10)	0.1358 (2)	0.3901 (2)	H3B	0.490 (1)	0.161 (2)	0.405 (2)
C3	0.43765 (10)	0.2412 (3)	0.4069 (2)	H4A	0.423 (1)	0.344 (2)	0.218 (2)
C4	0.44407 (10)	0.3907 (2)	0.3108 (2)	H4B	0.512 (1)	0.417 (2)	0.318 (2)
C5	0.39317 (10)	0.5668 (2)	0.3249 (2)	H5A	0.381 (1)	0.568 (2)	0.412 (2)
C6	0.30576 (11)	0.6027 (2)	0.2299 (2)	H5B	0.436 (1)	0.663 (2)	0.321 (2)
C7	0.22097 (11)	0.6731 (2)	0.2788 (2)	H6A	0.288 (1)	0.499 (2)	0.175 (2)
C8	0.16294 (10)	0.5608 (2)	0.3592 (2)	H6B	0.318 (1)	0.691 (2)	0.173 (1)
C9	0.11791 (9)	0.3912 (2)	0.2935 (1)	H7A	0.175 (1)	0.712 (2)	0.202 (2)
C10	0.17293 (9)	0.2198 (2)	0.3224 (1)	H7B	0.240 (1)	0.782 (2)	0.331 (2)
C11	0.26353 (10)	0.3690 (2)	0.4996 (1)	H8	0.110 (1)	0.641 (2)	0.367 (1)
C12	0.21171 (10)	0.5115 (2)	0.4873 (1)	H9	0.100 (1)	0.411 (2)	0.199 (2)
C13	0.12150 (10)	0.1182 (2)	0.4081 (1)	H10	0.174 (1)	0.151 (2)	0.250 (1)
C14	0.03133 (10)	0.3558 (2)	0.3460 (2)	H11	0.295 (1)	0.324 (2)	0.578 (2)
				H12	0.201 (1)	0.589 (2)	0.548 (2)

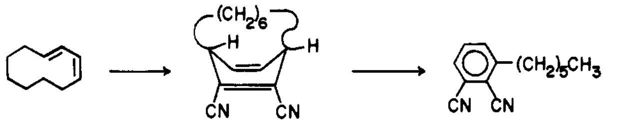
Thermal anisotropic refinement was applied to all nonhydrogen atoms. The positions of all hydrogen atoms were calculated and refined by full-matrix least-squares analysis. The *R* factor for the structure was 0.037. Figure 1 is an ORTEP drawing of **5** with all hydrogens except H-1 omitted for clarity. Table I lists the C–C and C–O bond lengths and the associated bond angles and Table II lists the atomic coordinates of all atoms. As can be seen from Table I, the effect of the internal hydrogen is to significantly distort the six-carbon chain which reaches from one side of the cyclohexene ring to the other. This distortion is reflected both in modified bond angles and slightly elongated C–C bond lengths. Of special interest are the C_1–C_2–C_3 and C_6–C_7–C_8 bond angles which are 107.8° and 123.9°, respectively. In the C_1–C_2–C_3 angle the chain is being sharply turned which results in a reduction of the "normal" C–C–C bond angle. In contrast, the C_6–C_7–C_8 bond angle is being "stretched" around the intruding hydrogen resulting in a significant enlargement of the C–C–C bond angle. Interestingly, the stretching of the six-carbon chain results in the other four C–C–C bond angles in this chain averaging 117.6°.

In order to determine whether these bond distortions would be reflected in thermal stability, we electrochemically bisdecarboxylated **4** in 10% aqueous pyridine with platinum electrodes to obtain 17% of **6**; ^{1}H NMR (C_6D_6) δ 6.23 (2 H, d of d of d, J = 1, 3, and 8 Hz), 5.94 (2 H, d of t, J = 2 and 8 Hz), 3.17 (1 H, m), 2.91 (1 H, m), 1.79–1.10 (12 H, m); ^{13}C NMR ($CDCl_3$) δ 138.7 (2 C), 131.6 (2 C), 40.3, 37.0, 32.1, 31.6, 30.9, 29.9, 29.1, 28.3. Heating of a benzene solution of **6** to 165 °C for 8 h resulted in the formation of **7** in 96% isolated yield. The IR and NMR spectra of **7** were identical with those in the literature.[9]



4 **6** **7**

The generality of the thermal conversion of **6** into **7** was confirmed by the addition of dicyanoacetylene to **3** which gave 6% of **8**; mp 68–70 °C; ^{1}H NMR (C_6D_6) δ 5.52 (1 H, d of d of d, J = 1, 3, and 7 Hz), 5.25 (1 H, d of d of d, J = 1, 6, and 7 Hz), 3.06 (1 H, m), 2.70 (1 H, m), 2.10–0.60 (12 H, m); ^{13}C NMR ($CDCl_3$) δ 136.4, 135.8, 130.6, 129.9, 115.0, 112.9, 44.6, 39.2, 31.2, 30.5, 30.0, 28.4, 27.8, and 27.3. Heating of **8** to 165 °C for 8 h gave an 81% isolated yield of **9**, which was identified by comparison of its spectra with those of **7**.



3 **8** **9**

In summary, we have prepared the first example of an (i,o)-bicyclo[6.2.2]dodecene derivative and demonstrated that it possessed considerable distortion of its C–C bond properties. We are continuing to explore the chemistry of this system and of other strained derivatives of this general class of compounds.

Acknowledgment. We are indebted to the National Science Foundation for Grant CHE78-10231 which supported this investigation and for Grant CHE77-28505 which aided in the purchase of an Enraf–Nonius X-ray diffractometer. We thank Professors L. Pignolet and J. Gougoutas and Mr. M. McGuiggan for assistance in the X-ray study.

Supplementary Material Available: Tables of bond distances, bond angles, and atom coordinates and an ORTEP drawing of **5** (24 pages). Ordering information is given on any current masthead page.

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(8) All calculations were carried out on a PDP 11/34 computer using the Enraf–Nonius SDP programs. This crystallographic computing package is described by B. A. Frentz, in "Computing in Crystallography", H. Schenck, R. Olthof-Hazekamp, H. van Konigweld, and G. S. Bassie, Eds., Delft University Press, Delft, Holland, 1978, pp 64–71.

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High Methane Formation during the Temperature-Programmed Decomposition in Flowing Hydrogen of Supported Mononuclear and Polynuclear Carbonyl Complexes

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Supported carbonyl complexes are currently receiving wide attention both for their potential applications as an important new class of catalysts and for their utility as models for more traditional types of heterogeneous catalysts.[1-6] Temperature-programmed

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