sample was diluted with CH_3CN, filtered, and analyzed by HPLC (condition B was used for the reaction of diazoindene with isobutene; condition C was used for the reaction of diazocyclopentadiene with isobutene). In the dilution experiments, a known mixture of 1,2-dichlorotetrafluoroethane and isobutene together with 40 mg of diazoindene was prepared in a Pyrex tube. The mixture was degassed and photolyzed as described above. The excess olefin was evaporated. The residue was diluted and analyzed by HPLC (condition B).

Control Experiments. *cis*- and *trans*-2-butenes were examined before and after photolysis by GC on a 7 ft × 0.25 in. 40% $AgNO_3$ on 45/60 GCR column at 40 °C. In each case the olefins were greater than 99% pure. The stereochemical stability of the cyclopropane adducts to the photolysis conditions was tested by adding a known mixture of **5b**-*syn*, **5b**-*anti*, and **5c** to a mixture of *trans*-4-methyl-2-pentene and diazoindene and then irradiating the mixture under standard reaction conditions. HPLC analysis showed no change in the cyclopropane distribution after irradiation. Similar control experiments were performed with mixtures of alkene and cyclopropane products from the reactions of diazoindene and diazocyclopentadiene with isobutene. In each case the products were found to be stable to the photolysis conditions.

Acknowledgments. We are grateful to the National Science Foundation for financial support. We sincerely thank Dr. Byron H. Arison of Merck, Sharp, and Dohme Research Laboratories, Rahway, NJ, for 300-MHz proton NMR spectra, for assistance with their interpretation, and for the NOE experiments. We also thank Prof. Joseph D. Rosen (Food Science Department, Cook College, Rutgers University) for the mass spectra and D. Silver for technical assistance.

Registry No. 1, 4729-01-5; **2**, 82539-36-4; **5a**, 60584-81-8; **5b**-*syn*, 86436-88-6; **5b**-*anti*, 86495-12-7; **5c**, 86495-13-8; **6a**, 86436-89-7; **6b**, 86436-90-0; **6c**, 86436-91-1; **8**, 24321-67-3; **9**, 86436-92-2; diazacyclopentadiene, 1192-27-4; diazoindene, 35847-40-6; isobutene, 115-11-7; *cis*-butene, 590-18-1; *trans*-butene, 624-64-6.

X-ray and Theoretical Analysis of the Relationship between Substituent Steric Effects and the Structure of Bicyclo[1.1.0]butane. The Unexpected Flexibility of the Bicyclo[1.1.0]butane Skeleton

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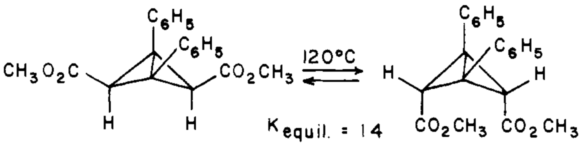
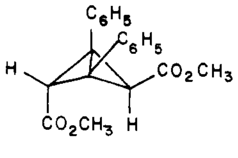
Abstract: Single-crystal X-ray analyses have been run for the three possible stereoisomers of 1,3-diphenyl-2,4-bis(methoxycarbonyl)bicyclo[1.1.0]butane. The endo–endo, exo–endo, and exo–exo diester interflap angles were 127.2°, 121.2°, and 113.4°, respectively, which showed surprising flexibility in the bicyclo[1.1.0]butane skeleton. As the interflap angle decreased, the C1–C3 bond lengths shortened (1.558, 1.498, and 1.455 Å, respectively). The bridgehead phenyl groups moved closer together as the interflap angle increased. This counter-intuitive movement of the bridgehead substituents necessitated that a least-motion discontinuity was required for any process involving flap inversion of the bicyclo[1.1.0]butane skeleton. In order to evaluate this relationship of bridgehead substituent position to the interflap angle of the bicyclo[1.1.0]butane skeleton, a theoretical study of the relationship between the interflap angle and the other bonding parameters was carried out for bicyclo[1.1.0]butane with both fully optimized HF-SCF and a generalized valence bond (GVB) approach in the PRDDO approximation. These calculations covered the range of interflap angles from 99° to 180° (planar bicyclo[1.1.0]butane). Our calculations corroborate the experimentally determined structural relationships and extend beyond what is experimentally determined. Discontinuity occurred at an interflap angle of 150 ± 2°, where the bridgehead substituents ceased their inward migration and subsequently moved outward as the interflap angle proceeded from 150° to 180°. At an interflap angle of 180°, the molecule lacked D_{2h} symmetry with the bridgehead hydrogens being out of the four-carbon plane by approximately 30°. The inversion barrier for a shift of these bridgehead hydrogens from one side of the four-carbon plane to the other side was calculated to be 4 kcal/mol.

Highly strained, polycyclic molecules have attracted considerable attention during the last two decades.[3] Both experimental and theoretical studies have emphasized the unique properties of this class of compounds. Because of its unique chemical reactivity and supposedly rigid structure, the bicyclo[1.1.0]butane system has received the most attention. Among the relatively large number of examples of anomolous behavior noted for this bicyclic ring system was a study of its flap inversion by Woodward and Dalrymple.[4] These workers reported that the stereoisomers **1** and **2** were interconverted at 120 °C.[5] Most curious about this report[4] was the finding that the diendo isomer, **2**, was the thermodynamically more stable component of the equilibrium mixture.



1 **2**



3

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(1) Lando Undergraduate Fellow, summer 1975.

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(3) For a leading reference see: Greenberg, A.; Liebman, J. F. "Strained Organic Molecules"; Academic Press: New York, 1978.

(4) Woodward, R. B.; Dalrymple, D. L. *J. Am. Chem. Soc.* **1969**, *91*, 4612.

(5) D'yakonov, I. A.; Razen, V. V.; Komendantov, M. I. *Tetrahedron Lett.* **1966**, 1127, 1135.

0002-7863/83/1505-5865$01.50/0

Table I. Crystallographic Data for Compounds 1, 2, and 3

property	1	2	3
a, Å	11.454 (3)	17.48 (1)	8.939 (3)
b, Å	18.018 (5)	9.121 (4)	12.972 (4)
c, Å	16.620 (4)	21.20 (1)	15.047 (6)
β, deg		90.21 (4)	
space group	*Pbca*	*C*2/*c*	$P2_12_12_1$
z	8	8	4
$\rho_c{}^a$	1.248	1.267	1.227
$\rho_m{}^a$	1.25	1.27	1.23
R^b	0.040	0.045	0.050
$R_w{}^c$	0.044	0.059	0.064
U^d	1.49	1.61	1.46
P^e	0.04	0.05	0.06
NO^f	806	1783	1113
NT^g	1139	2211	1385

[a] The calculated and measured crystal densities in g cm^{-3}. [b] Conventional *R* factor. [c] Weighted *R* factor. [d] Error in observation of unit weight. [e] Weighting parameter. [f] Number of "observed" reflections used in the refinements. [g] Number of unique measured reflections.

Since it had been suggested that even two hydrogens in the endo position at C2 and C4 would sterically interact,[6] the finding that **2** was more stable than **1**[4] suggested to us that a detailed study of the structures of **1**, **2**, and **3** was merited. We now wish to report the details of single-crystal X-ray structure determinations of these three isomers.[7] The results of this study indicate that considerable flexibility exists in the bicyclo[1.1.0]butane skeleton. As a result, we have carried out, and also report here, an extensive theoretical evaluation of flap angle variation and inversion for this system. These calculations extend and complement those published recently by Paddon-Row[8] that evaluate only a small range of interflap angle. We have focused on interflap angles of 99°–180° while Paddon-Row et al. studied angles of 93–123°. Our extension of these earlier calculations[8] allowed us to conclude that a non-least-motion movement of the bridgehead substituents is associated with any process involving inversion of the bicyclo[1.1.0]butane envelope.

In terms of useful structural data, our preliminary reports[7,9] and the reports of Irngartinger[10] and of Schaefer and Trotter[11] represent the major X-ray studies of derivatives of bicyclo[1.1.0]butane.[12] The investigations of Irngartinger[10] and Trotter[11] involved bridged derivatives of bicyclo[1.1.0]butane, in which the structure of the bicyclo[1.1.0]butane moiety of these tricyclic molecules was governed in large part by the nature of the carbon chains that joined the endo-2 and endo-4 positions of the bicyclo[1.1.0]butane moiety. Thus, the influence of substituents on structure could best be assessed in nonbridged systems such as **1**–**3**.

Experimental Section

Table II. Fractional Atomic Coordinates for 1

atom	*x*	*y*	*z*
O1	0.2428 (3)	0.5160 (2)	−0.0975 (2)
O2	0.4326 (3)	0.5461 (2)	−0.1095 (2)
O3	0.2122 (3)	0.2350 (2)	0.0044 (2)
O4	0.3910 (3)	0.1953 (2)	0.0395 (2)
C1	0.3194 (4)	0.3858 (2)	−0.0036 (3)
C2	0.3927 (4)	0.4279 (2)	−0.0645 (3)
C3	0.3265 (4)	0.3572 (2)	−0.0853 (2)
C4	0.3804 (4)	0.3119 (2)	−0.0194 (3)
C5	0.2327 (4)	0.4096 (2)	0.0563 (2)
C6	0.2701 (4)	0.4524 (3)	0.1210 (3)
C7	0.1915 (5)	0.4757 (3)	0.1797 (3)
C8	0.0759 (5)	0.4572 (3)	0.1728 (3)
C9	0.0374 (5)	0.4150 (3)	0.1098 (3)
C10	0.1157 (5)	0.3922 (3)	0.0518 (3)
C11	0.2543 (4)	0.3335 (2)	−0.1548 (2)
C12	0.2902 (4)	0.2737 (2)	−0.2013 (3)
C13	0.2234 (5)	0.2510 (3)	−0.2680 (3)
C14	0.1251 (5)	0.2886 (3)	−0.2882 (3)
C15	0.0899 (5)	0.3471 (3)	−0.2432 (3)
C16	0.1525 (4)	0.3702 (3)	−0.1761 (3)
C17	0.3434 (4)	0.5005 (2)	−0.0917 (2)
C18	0.3996 (5)	0.6207 (3)	−0.1345 (3)
C19	0.3165 (4)	0.2441 (3)	0.0084 (3)
C20	0.3446 (5)	0.1269 (3)	0.0708 (3)
H2	0.474 (3)	0.425 (2)	−0.060 (2)
H4	0.458 (3)	0.308 (2)	−0.007 (2)
H6	0.361 (4)	0.465 (2)	0.128 (2)
H10	0.090 (4)	0.359 (2)	0.007 (2)
H12	0.357 (3)	0.245 (2)	−0.184 (2)
H16	0.132 (4)	0.412 (2)	−0.145 (2)

Dimethyl 1,3-Diphenylbicyclo[1.1.0]butane-*exo*,*exo*-2,4-dicarboxylate (1), Dimethyl 1,3-Diphenylbicyclo[1.1.0]butane-*endo*,*endo*-2,4-dicarboxylate (2), and Dimethyl 1,3-Diphenylbicyclo[1.1.0]butane-*exo*,-*endo*-2,4-dicarboxylate (3). These compounds were prepared according to the literature procedures[4,5] and exhibited spectral properties and melting points that corresponded with those reported.[4,5]

X-ray Diffraction Studies. The unit cell parameters (Table I) for each structure were obtained through a least-squares analysis of the experimental diffractometer settings of at least 15 reflections with $2\theta > 70°$ using Cu Kα monochromatic radiation (λ = 1.5418 Å). Space groups were assigned on the basis of systematic absences on Weissenberg photographs. The crystal densities were measured by flotation in petroleum ether–carbon tetrachloride mixtures. Intensities were measured on a Syntex P2$_1$ diffractometer at 23 °C with the θ–2θ variable scan rate technique. They were corrected only for the Lorentz–polarization factors. The structures were solved by direct methods and refined by full-matrix least-squares analysis[13] on the basis of "observed" reflections for which $I > 2\sigma(I)$.

The phenyl and tertiary hydrogens as well as at least one of the hydrogens of each ester methyl group were evident in difference maps. The scattering from all of the hydrogens was taken into account in the terminal stages of refinement. However, only the coordinates of the two tertiary hydrogens, which were attached directly to C2 and C4 of the bicyclo[1.1.0]butane skeleton, were allowed to vary; the methyl hydrogens and the hydrogens on the aryl groups were fixed at idealized positions. The least-squares weights, $\omega = \sigma^{-2}(F_o)$, were calculated with the assumption that $\sigma^{-2}(I) = \epsilon^2 + (pI)^2$ where ϵ is a statistical counting error and $0.04 \leq p \leq 0.06$. The refinements, assuming anisotropic motion for all C and O atoms, converged to $R \leq 0.05$ (see Table I). The fractional atomic coordinates and errors from the least-squares refinements are given in Tables II, III, and IV. Bond distances and angles are presented in Tables V and VI. Average deviations from the least-squares planes of the phenyl rings were consistent with the estimated errors in bond length. Tables of the anisotropic thermal parameters and observed and calculated structure factors are included as supplementary material.

Computational Methods. All calculations were done in the partial retention of diatomic differential overlap (PRDDO) approximation.[14,15] PRDDO is an approximate molecular orbital method that employs a minimum basis set of Slater-type orbitals and that yields results that agree closely with those obtained from ab initio methods with the same basis set.[15] The orbital exponents for carbon [$\xi(1s) = 5.67$, $\xi(2s) = \xi(2p) = 1.72$] were taken from a standard compilation,[16] while the value for

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(6) Blanchard, E. P., Jr.; Cairncross, A. *J. Am. Chem. Soc.* **1966**, *88*, 487, 496.

(7) For a preliminary report of a portion of our X-ray studies see: Gougoutas, J. Z. *Cryst. Struct. Commun.* **1977**, *8*, 131, 135.

(8) Paddon-Row, M. N.; Houk, K. N.; Dowd, P.; Garner, P.; Schappert, R. *Tetrahedron Lett.* **1981**, *22*, 4799.

(9) Gassman, P. G.; Mullins, M. J. *Tetrahedron Lett.* **1979**, 4457.

(10) Irngartinger, H.; Lukas, K. L. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 694. Irngartinger, H.; Lukas, K. L.; Goldman, A. *Fresenius Z. Anal. Chem.* **1980**, *304*, 269. Irngartinger, H.; Goldmann, A.; Schappert, R.; Garner, P.; Dowd, P. *J. Chem. Soc., Chem. Commun.* **1981**, 455. Dowd, P.; Garner, P.; Schappert, R.; Irngartinger, H.; Goldman, A. *J. Org. Chem.* **1982**, *47*, 4240.

(11) Trotter, J.; Gibbons, C. S.; Nakatsuka, N.; Masamune, S. *J. Am. Chem. Soc.* **1967**, *89*, 2792. Johnson, P. L.; Schaefer, J. P. *J. Org. Chem.* **1972**, *37*, 2762.

(12) For additional structural data see: Harmony, M. D.; Cox, K. *J. Am. Chem. Soc.* **1966**, *88*, 5048. Haller, I.; Srinivasan, R. *J. Chem. Phys.* **1964**, *41*, 2745. Cox, K. W.; Harmony, M. D.; Nelson, G.; Wiberg, K. B. *Ibid.* **1969**, *50*, 1976.

(13) The parameters for **2** and **3** that were presented in preliminary reports[7] were derived from block-diagonal least-squares refinements.

(14) Halgren, T. A.; Lipscomb, W. N. *J. Chem. Phys.* **1973**, *58*, 1569.

(15) Halgren, T. A.; Kleier, D. A.; Hall, J. H., Jr.; Brown, L. D.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1978**, *100*, 6595.

(16) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657.

Table III. Fractional Atomic Coordinates for **2**

atom	*x*	*y*	*z*
O1	0.1385 (1)	0.6564 (2)	0.06948 (9)
O2	0.0142 (1)	0.6033 (2)	0.06411 (8)
O3	0.1955 (1)	0.3875 (2)	0.00939 (8)
O4	0.2912 (1)	0.4580 (2)	0.07200 (8)
C1	0.1541 (1)	0.4246 (3)	0.1715 (1)
C2	0.0839 (1)	0.4746 (3)	0.1384 (1)
C3	0.1066 (1)	0.3167 (3)	0.1301 (1)
C4	0.1908 (1)	0.3356 (3)	0.1200 (1)
C5	0.1681 (1)	0.4253 (3)	0.2398 (1)
C6	0.2131 (2)	0.3190 (3)	0.2686 (1)
C7	0.2229 (2)	0.3188 (4)	0.3334 (1)
C8	0.1894 (2)	0.4251 (4)	0.3699 (1)
C9	0.1463 (2)	0.5325 (4)	0.3424 (1)
C10	0.1353 (1)	0.5321 (3)	0.2777 (1)
C11	0.0635 (1)	0.1844 (3)	0.1458 (1)
C12	0.1007 (2)	0.0498 (3)	0.1498 (1)
C13	0.0606 (2)	−0.0748 (3)	0.1635 (2)
C14	−0.0170 (2)	−0.0694 (3)	0.1724 (2)
C15	−0.0547 (2)	0.0621 (4)	0.1688 (2)
C16	−0.0145 (2)	0.1878 (3)	0.1557 (1)
C17	0.0841 (1)	0.5867 (3)	0.0869 (1)
C18	0.0047 (2)	0.7106 (3)	0.0143 (1)
C19	0.2242 (1)	0.3975 (3)	0.0604 (1)
C20	0.3312 (2)	0.5202 (5)	0.0189 (2)
H2	0.040 (1)	0.483 (3)	0.164 (1)
H4	0.220 (1)	0.256 (3)	0.135 (1)
H6	0.237 (0)	0.245 (0)	0.243 (0)
H10	0.105 (0)	0.606 (0)	0.259 (0)
H12	0.154 (0)	0.045 (0)	0.143 (0)
H16	−0.040 (0)	0.280 (0)	0.153 (0)

Table IV. Fractional Atomic Coordinates for 3

atom	*x*	*y*	*z*
O1	0.1484 (4)	0.5490 (3)	0.1286 (3)
O2	−0.0450 (4)	0.4526 (3)	0.0824 (2)
O3	0.2150 (4)	0.3017 (4)	0.3760 (3)
O4	0.0120 (4)	0.2890 (3)	0.4596 (2)
C1	−0.0821 (5)	0.3791 (3)	0.2597 (3)
C2	0.0640 (5)	0.4119 (4)	0.2201 (3)
C3	0.0134 (5)	0.3009 (3)	0.2133 (3)
C4	−0.0279 (5)	0.2854 (3)	0.3089 (3)
C5	−0.2322 (5)	0.4250 (3)	0.2537 (3)
C6	−0.3595 (6)	0.3659 (4)	0.2552 (4)
C7	−0.5017 (6)	0.4105 (5)	0.2525 (4)
C8	−0.5128 (6)	0.5171 (5)	0.2468 (4)
C9	−0.3882 (6)	0.5749 (5)	0.2458 (4)
C10	−0.2477 (6)	0.5309 (4)	0.2487 (4)
C11	0.0045 (5)	0.2305 (4)	0.1372 (3)
C12	−0.1021 (6)	0.1549 (4)	0.1332 (4)
C13	−0.1085 (9)	0.0849 (5)	0.0633 (4)
C14	−0.0007 (11)	0.0922 (5)	−0.0049 (4)
C15	0.1052 (10)	0.1657 (5)	0.0009 (5)
C16	0.1088 (7)	0.2337 (5)	0.0698 (4)
C17	0.0635 (6)	0.4784 (4)	0.1403 (3)
C18	−0.0569 (10)	0.5121 (5)	0.0034 (4)
C19	0.0840 (6)	0.2921 (4)	0.3827 (3)
C20	0.1016 (8)	0.2970 (5)	0.5389 (4)
H2	0.137 (5)	0.428 (4)	0.262 (3)
H4	−0.101 (5)	0.229 (4)	0.315 (3)
H6	−0.353 (0)	0.292 (0)	0.256 (0)
H10	−0.162 (0)	0.574 (0)	0.248 (0)
H12	−0.175 (0)	0.149 (0)	0.178 (0)
H16	0.192 (0)	0.282 (0)	0.071 (0)

Table V. Bond Distances and Their Least-Squares Estimated Errors for 1, **2**, and 3 in Å

bond	1	2	3
C1–C2	1.517 (7)	1.484 (3)	1.498 (6)
C1–C3	1.455 (7)	1.558 (3)	1.498 (6)
C1–C4	1.527 (7)	1.506 (3)	1.504 (6)
C1–C5	1.470 (7)	1.467 (3)	1.471 (6)
C2–C3	1.522 (6)	1.505 (3)	1.513 (6)
C2–C17	1.495 (8)	1.495 (3)	1.478 (6)
C2–H2	0.94 (5)	0.94 (2)	0.93 (4)
C3–C4	1.498 (6)	1.497 (3)	1.498 (5)
C3–C11	1.484 (6)	1.462 (3)	1.468 (6)
C4–C19	1.497 (7)	1.505 (3)	1.497 (6)
C4–H4	0.92 (4)	0.94 (2)	0.99 (5)
C5–C6	1.391 (6)	1.387 (3)	1.372 (6)
C5–C10	1.378 (6)	1.388 (3)	1.383 (6)
C6–C7	1.392 (7)	1.386 (3)	1.397 (7)
C7–C8	1.370 (7)	1.372 (4)	1.389 (8)
C8–C9	1.367 (7)	1.365 (4)	1.343 (8)
C9–C10	1.381 (7)	1.384 (3)	1.380 (7)
C11–C12	1.388 (6)	1.392 (3)	1.368 (6)
C11–C16	1.388 (6)	1.380 (3)	1.377 (6)
C12–C13	1.407 (7)	1.367 (3)	1.390 (8)
C13–C14	1.356 (6)	1.370 (4)	1.411 (10)
C14–C15	1.353 (7)	1.371 (4)	1.347 (10)
C15–C16	1.390 (6)	1.374 (3)	1.362 (9)
C17–O1	1.190 (6)	1.204 (2)	1.203 (5)
C17–O2	1.344 (6)	1.322 (2)	1.346 (5)
C18–O2	1.458 (5)	1.449 (3)	1.421 (5)
C19–O3	1.208 (5)	1.195 (2)	1.181 (6)
C19–O4	1.331 (6)	1.317 (2)	1.325 (6)
C20–O4	1.440 (6)	1.443 (3)	1.440 (6)

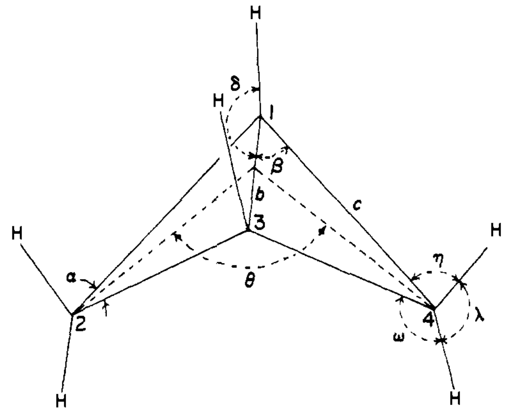

Figure 1. Labeled model of bicyclo[1.1.0]butane indicating the designations for angles and bond lengths used in the theoretical calculations.

$\xi(1s)$ for hydrogen was set at 1.2. Geometry optimization was carried out at given flap angles, ($\theta = \theta_{opt} + X$) and all geometry parameters were subsequently optimized in C_{2v} symmetry except for the C–H bond distances. These C–H bond lengths were those used for a fully optimized HF-SCF calculation on bicyclo[1.1.0]butane at its optimized flap angle of θ_{opt} = 118.9° (C1–H = 1.071 Å, C2–H = 1.093 Å).[12] The labeling convention for these calculations is given in Figure 1. There was significant coupling between *b* (the C1–C3 bond), *c* (the C1–C2 bond), and θ.

Initially, calculations were performed by using a single determinant RHF wave function. Since we were evaluating an approach to "breaking" of the C1–C3 bond in the inversion process, it was decided that an improved form for the wave function would be to describe this bond in the generalized valence bond (GVB) framework.[17] Rather than describing the bridgehead bonding electron pair by the orbital $\phi_n(1)\phi_n(2)$, each electron was allowed to occupy its own orbital $[\phi_A(1)\phi_B(2) + \phi_B(1)\phi_A(2)]$, and these two new orbitals were solved to self-consistency. These two orbitals were constrained to remain singlet coupled, and the spin couplings were not optimized. The GVB orbitals remained orthogonal to the remaining orbitals. This corresponded to calculating the GVB wave function with both perfect-pairing and strongly orthogonal restrictions. The GVB calculations were performed for values of θ from θ_{opt} − 10° to θ_{opt} + 61.1°, where the C1–C3 bond was the HOMO, and its antibonding counterpart was the LUMO. These two orbitals were highly localized even in the canonical molecular orbital sense.

Discussion of Results

X-ray Structural Results. In order to compare the molecular geometries of **1**, **2**, and **3**, we felt that it would be useful to regard the differences in their observed structures as distortions from a hypothetical "standard" structure having C_{2v} symmetry in which

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(17) Goddard, W. A., III; Dunning, T. H., Jr.; Hunt, W. J.; Hay, P. J. *Acc. Chem. Res.* **1973**, *6*, 368.

Table VI. Bond Angles and Their Least-Squares Estimated Errors for 1, 2, and 3 in Degrees

angle	**1**	**2**	3
C2–C1–C3	61.6 (3)	59.2 (1)	60.7 (3)
C2–C1–C4	93.9 (4)	100.1 (2)	98.3 (3)
C2–C1–C5	132.8 (4)	126.9 (2)	131.0 (4)
C3–C1–C4	60.2 (3)	58.5 (1)	59.9 (3)
C3–C1–C5	140.6 (5)	130.2 (2)	140.0 (4)
C4–C1–C5	132.9 (4)	130.4 (2)	130.6 (4)
C1–C2–C3	57.2 (3)	62.8 (1)	59.7 (3)
C1–C2–C17	115.4 (5)	123.5 (2)	119.1 (4)
C1–C2–H2	118 (3)	115 (1)	114 (3)
C3–C2–C17	118.5 (5)	124.6 (2)	120.0 (4)
C3–C2–H2	118 (3)	111 (1)	118 (3)
C17–C2–H2	117 (3)	112 (1)	115 (3)
C1–C3–C2	61.2 (3)	58.0 (1)	59.6 (3)
C1–C3–C4	62.3 (3)	59.0 (1)	60.2 (3)
C1–C3–C11	143.0 (5)	131.8 (2)	139.0 (4)
C2–C3–C4	94.9 (4)	99.6 (2)	97.9 (3)
C2–C3–C11	134.0 (4)	128.8 (2)	131.4 (4)
C4–C3–C11	130.0 (4)	129.4 (2)	130.8 (4)
C1–C4–C3	57.5 (3)	62.5 (1)	59.9 (3)
C1–C4–C19	115.7 (5)	125.0 (2)	122.3 (4)
C1–C4–H4	118 (3)	114 (1)	116 (3)
C3–C4–C19	117.9 (5)	123.2 (2)	122.6 (4)
C3–C4–H4	127 (3)	114 (1)	111 (3)
C19–C4–H4	110 (3)	111 (1)	115 (3)
C1–C5–C6	118.5 (7)	121.5 (2)	121.9 (4)
C1–C5–C10	123.6 (6)	120.4 (2)	119.8 (4)
C6–C5–C10	117.9 (5)	118.1 (2)	118.3 (4)
C5–C6–C7	120.7 (5)	120.4 (2)	121.5 (5)
C6–C7–C8	119.5 (5)	120.4 (2)	118.6 (5)
C7–C8–C9	120.8 (6)	120.2 (2)	119.8 (5)
C8–C9–C10	119.4 (6)	119.7 (2)	121.6 (5)
C5–C10–C9	121.7 (6)	121.2 (2)	120.3 (5)
C3–C11–C12	119.5 (6)	120.1 (2)	121.2 (4)
C3–C11–C16	122.0 (5)	121.8 (2)	121.3 (5)
C12–C11–C16	118.5 (5)	118.2 (2)	117.4 (4)
C11–C12–C13	120.2 (5)	120.5 (2)	122.0 (5)
C12–C13–C14	120.1 (5)	120.5 (3)	118.5 (6)
C13–C14–C15	120.0 (6)	120.0 (2)	118.7 (6)
C14–C15–C16	121.6 (6)	119.6 (2)	121.6 (6)
C11–C16–C15	119.7 (5)	121.2 (2)	121.7 (6)
C2–C17–O1	126.6 (7)	126.1 (2)	124.1 (4)
C2–C17–O2	108.3 (6)	109.9 (2)	112.6 (4)
O1–C17–O2	125.1 (7)	123.9 (2)	123.3 (4)
C17–O2–C18	115.4 (5)	116.6 (2)	117.5 (4)
C4–C19–O3	125.4 (6)	124.6 (2)	127.2 (5)
C4–C19–O4	110.2 (5)	110.5 (2)	108.7 (4)
O3–C19–O4	124.5 (6)	124.9 (2)	124.0 (5)
C19–O4–C20	118.0 (4)	116.9 (2)	116.8 (4)

all atoms but the C2 and C4 substituents are contained in two planes (Figure 2): plane P1 contains atoms C1, C2, C4, the phenyl carbon atoms C5–C10 (and their attached hydrogens); plane P2 contains atoms C2, C3, C4, the phenyl carbon atoms C11–C16 (and their attached hydrogens). The C–C bond lengths around the periphery of the bicyclo[1.1.0]butane skeleton, c, are initially set at 1.505 Å, which is the average of the twelve observed values in **1**, **2**, and **3**. The C1–C3 bond, b, is formed through increasing what is essentially the overlap of the p orbitals. This occurs as the dihedral angle between planes P1 and P2, which we have labeled as the folding angle, τ, is decreased from its value of 180° in a square-planar diradical structure (γ = C2–C1–C4 angle = 90°). The length of b is given by $b = 2c \sin(\tau/2) \cos(\gamma/2)$.

The interflap angle, θ, is the obtuse dihedral angle between the planes of the two cyclopropyl rings that are defined as plane P3, which contains C1, C2, and C3, and plane P4, which contains C1, C3, and C4. For our hypothetical "standard" structure, θ is related to the folding angle, τ, as $\cot(\theta/2) = \cos(\tau/2) \cot(\gamma/2)$. The C1–C2–C3 and C1–C4–C3 bond angles, α, are also dependent on τ and γ according to the relationship $\sin(\alpha/2) = \cos(\gamma/2) \sin(\tau/2)$, while the C2–C1–C3 bond angle, β, and all like it are defined by $\beta = 90 - \alpha/2$.

The substituents at C2 and C4 can be defined as endo and being within the flaps or as exo and being outside the flaps. These substituents in the examples being studied are either hydrogen or the carbonyl carbon of the methoxycarbonyl group (C17 at C2 and C19 at C4). When the two endo substituents are identical, the nonbonded distance, ϵ, between the two endo atoms directly bonded to C2 and C4, respectively, for our model is given by $\epsilon = 2[c \sin(\gamma/2) - H \sin(\kappa - \theta/2)]$ where H is the C2-endo atom bond length, and κ is the angular displacement of the endo atom from P3.

The geometric variations among the experimentally determined structures of **1**, **2**, and **3** are considered below in terms of the above "standard" model. For the exo–exo isomer, **1**, the folding was found experimentally to be perpendicular (τ = 89.8°). Perpendicular folding of the model (τ = 90°) led to a bicyclo[1.1.0]butane structure with all equal bond lengths $b = c = 1.505$ Å when γ = 90°. In addition, $\alpha = \beta = 60°$, and the interflap angle, θ, was 109.47°. This gave a relatively short endo–endo nonbonded distance of ϵ = 2.13 Å in the model, for two endo hydrogens assuming $\kappa = \theta/2 = 54.7°$ (parallel endo bonds). The observed nonbonded distance between H2 and H4 (both endo) was 2.29 (6) Å.[18] This value was longer than that of the model and resulted from a small elongation of c (average c = 1.516 Å) and an expansion of the angle, γ, to 94.4°. (Atoms C2 and C4 of the model move apart with the net effect of drawing the bridgehead atoms C1 and C3 closer together.) As a result, the bridging C1–C3 bond, b was shortened relative to the model [b_{obsd} = 1.455 (7) Å], while the interflap angle increased to θ_{obsd} = 113.4°. The observed angles, α and β, were contracted (57.4°) and expanded (61.3°), respectively, in comparison to the model. Since the observed κ does not vary from that of the model, the endo bonds are no longer parallel.

For the endo–endo isomer, **2**, comparison of the experimental structure was initially made with the model (τ = 90°). The larger groups in the endo position, relative to **1**, required an additional expansion of the nonbonded distance between the endo substituents of the model. For **2**, where the average c was 1.498 Å and H_{exo} = 1.500 Å, the distance between C17 and C19 was observed to be 3.050 (3) Å while the distance obtained from the model was 2.13 Å. Some expansion of the model was realized through further opening of γ to the observed value of 99.9° (ϵ_{calcd} = 2.53 Å, θ_{calcd} = 118.5°). Additional lengthening of ϵ to 2.76 Å gave $\alpha = \alpha_{\text{obsd}}$ = 62.6° and a relatively large observed interflap angle, θ, of 127.2°. As a result, the C1–C3 bond, b, became 1.558 (3) Å, and β = 58.7°. Finally, adjustment of the only remaining parameter of the model, κ, to 49.0° completed the expansion of ϵ_{calcd} to the observed value of 3.050 Å. This contraction of κ relative to the value of 54.7° in the model and in **1** effectively corresponded to an increase in the bond angles, ω, involving the endo substituents and the adjacent peripheral bonds (e.g., angle C1–C2–C17) according to $\cos \omega = -\cos \kappa \cos(\alpha/2)$. Thus, in **1**, where the endo substituents were hydrogens, the average ω was 120° while for **2** the average ω was 124°. The interflap angle θ and the bridge bond length b in **2** are, to date, the largest found for the bicyclo[1.1.0]butane nucleus.

The remarkably large difference (18°) in the observed folding angles of **1** and **2** is indicative of the considerable flexibility that is inherent in the bicyclo[1.1.0]butane nucleus. Not surprisingly, the exo–endo isomer **3** had an intermediate structure: b = 1.498 Å, c = 1.504 Å, τ = 98.9°, θ = 121.2°, α = 59.8°, β = 60.1°, γ = 98.1°, ϵ = 2.58 Å. It is of interest to note that despite the presence of four relatively large substituents, the geometry of the bicyclo[1.1.0]butane nucleus of **3** is essentially the same as that of the parent hydrocarbon: b = 1.497 Å, c = 1.498 Å, τ = 99.6°, θ = 121.7°, α = 60.0°, β = 60.0°, γ = 98.3°.[12c] (These parameters are summarized in Table VII.)

While it was not unexpected that the structure of the exo–endo isomer **3** would be intermediate between that of **1** and **2**, it seemed at first rather curious that it was the nucleus of **3**, and not the nucleus of the exo–exo isomer, **1**, whose skeleton had adopted the optimum, lowest energy structure of the parent hydrocarbon. The

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[18] This value is based on the uncorrected and probably underestimated average C2–H and C4–H bond lengths observed in these isomers (0.94 Å).

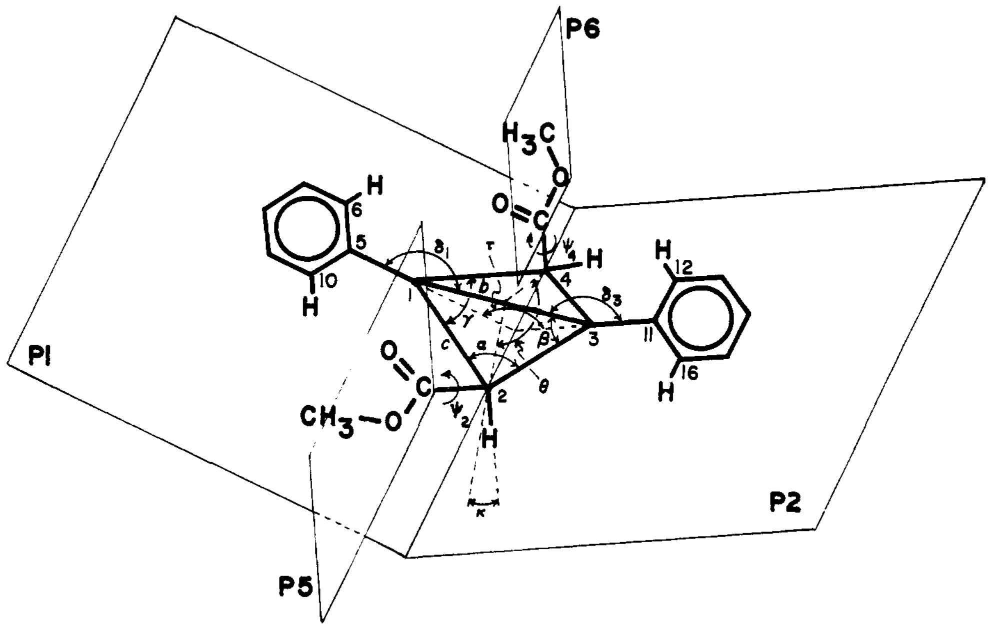

Figure 2. Representation of a hypothetical "standard" model of bicyclo[1.1.0]butane, based on 1,3-diphenyl-*exo,exo*-2,4-bis(methoxycarbonyl)bicyclo[1.1.0]butane. Planes, bond angles, bond lengths, and other angles are labeled as defined in the text.

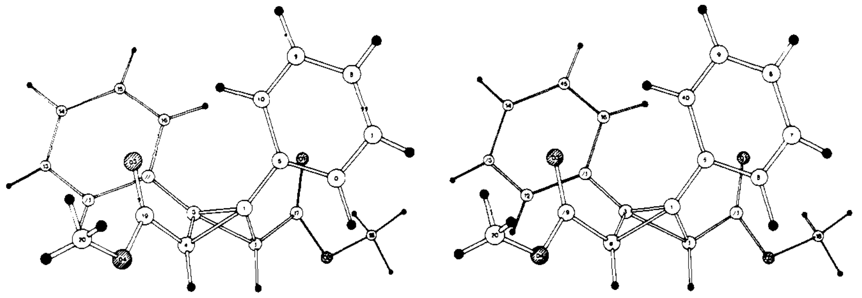

Figure 3. Computer-generated X-ray structural stereoview representation of 1,3-diphenyl-*exo,exo*-2,4-bis(methoxycarbonyl)bicyclo[1.1.0]butane (**1**).

bicyclo[1.1.0]butane nucleus of **1** was folded 8.1° ($\Delta\tau$) *more* than the parent nucleus while the nucleus of **2** was folded 9.9° ($\Delta\tau$) *less* than that of the parent. The basis for the increased pucker of **1** relative to the parent hydrocarbon became evident upon examining the conformational aspects of the methoxycarbonyl and phenyl substituents.

Conformational Aspects of the Methoxycarbonyl Groups. Since both ester groups in each structure have been found to adopt a virtually planar *S*-cis conformation about the C–O single bond, these groups can be conveniently described relative to our model by two planes. These are plane P5, which contains atoms O1, C17, O2, and C18, and plane P6, which contains atoms O3, C19, O4, and C20. The orientations of P5 and P6 relative to a plane through C2 and C4 that bisects the C1–C3 bond, *b*, can be characterized by the torsional angles ψ_2 (defined by O1–C17–C2–C4) and ψ_4 (defined by O3–C19–C4–C2), respectively. A model with $\psi_2 = \psi_4 = 0°$ for **1** is depicted in Figure 2. In fact, for structure **1**, $\psi_2 = -1.7°$ and $\psi_4 = +9.4$ (Figure 3). Thus, for this compound, P5 and P6 nearly bisected the C1–C3 bond. For the exo–exo isomer, **1**, there were no short transannular distances for the methoxycarbonyl groups.

A "bisecting" orientation, as observed for **1**, was not found for the endo–endo isomer, **2**, because transannular steric interactions should favor a more nearly "parallel" orientation where $\psi_2 = \psi_4 = 90°$ (Figure 4). The observed values for **2** were $\psi_2 = -45°$ and $\psi_4 = -68.7°$. The intermediate values for these angles may be the result of a transannular stabilizing donor–acceptor type of interaction between the carbonyl oxygen (O1) of one ester group and the carbonyl carbon (C19) of the transannular ester group (O1–C19 nonbonded distance = 2.803 Å; angles O1- -C19–O4 = 96.3°, O1- -C19–O3 = 84.4°, C17–O1- -C19 = 90°). The 0.020 (3) Å displacement of C19 toward O1 from the plane defined by O3, O4, and C4 was probably a consequence of this interaction.

Table VII. Bonding Parameters[a] for the Bicyclo[1.1.0]butane Derivatives 1, 2, and 3 As Determined from the Crystallographic Data

	1	2	3	parent hydrocarbon[12c]
b, Å	1.455	1.558	1.498	1.497
c_1, Å	1.524	1.505	1.509	1.498
c_2, Å	1.508	1.491	1.498	1.498
α, deg	57.4	62.6	59.8	60.0
β, deg	61.3	58.7	60.1	60.0
γ, deg	94.4	99.9	98.1	98.3
θ, deg	113.4	127.2	121.2	121.7
τ, deg	89.8	107.8	98.9	99.6
δ_1, deg	140.6	130.2	140.0	128.4
δ_3, deg	143.0	131.8	139.0	128.4

[a] The bonding parameters are defined in the text and are illustrated in Figure 2.

For the exo–endo isomer, **3**, the exo methoxycarbonyl group again adopted a "bisecting" orientation with $\psi_2 = 173.7°$ (Figure 5). The C17–O1 carbonyl group pointed away from the bicyclo[1.1.0]butane skeleton in contrast to the orientation of this group in **1**. As might be expected, the endo methoxycarbonyl group of **2**, which had $\psi_4 = -42.8°$, was neither in the "bisecting" nor in the "parallel" conformation.

Conformational Aspects of the Phenyl Groups. The conformations of the phenyl groups of **1**, **2**, and **3** were also of interest. The extent of rotation of each phenyl group about its bond to the bridgehead carbon atom can be characterized by a torsional angle (ϕ_1 is the C6–C5–C1–C3 torsional angle and ϕ_3 is the C12–

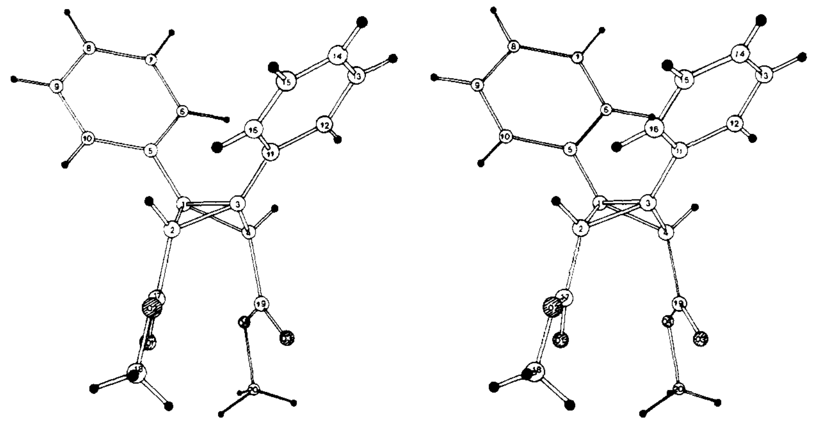

Figure 4. Computer-generated X-ray structural stereoview representation of 1,3-diphenyl-*endo,endo*-2,4-bis(methoxycarbonyl)bicyclo[1.1.0]butane (**2**).

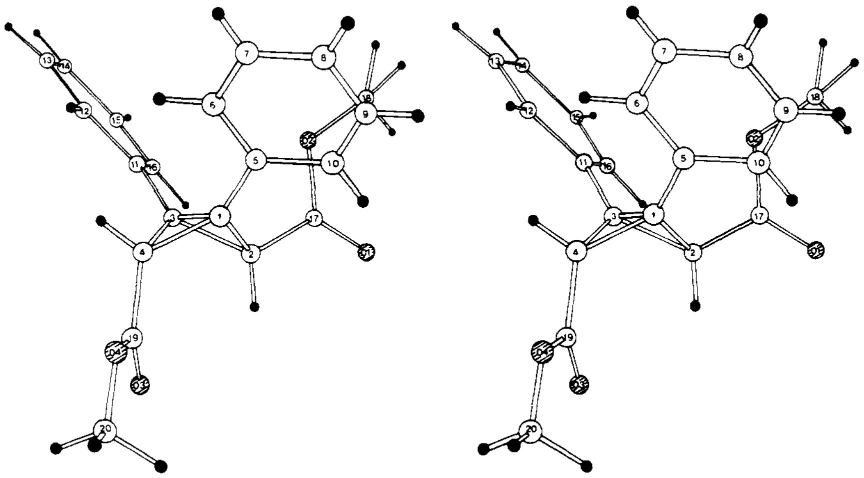

Figure 5. Computer-generated X-ray structural stereoview representation of 1,3-diphenyl-*exo,endo*-2,4-bis(methoxycarbonyl)bicyclo[1.1.0]butane (**3**).

C11–C3–C1 torsional angle). These torsional angles are influenced by steric interactions of the aromatic ortho hydrogens H6, H10, H12, and H16. Conformations in which the planes of the phenyl rings bisected the C2- - -C4 vector ($\phi_1 = \phi_3 = 0°$) were unfavorable in all isomers because of the steric interactions of the ortho hydrogens. For $\phi_1 = \phi_3 = 0°$, the transannular nonbonded distance for the ortho hydrogens on the two phenyl groups is greater than 2.4 Å only if τ is greater than 116°, in which case ϕ is greater than 124° (assuming a C1–C5 bond length of 1.48 Å). Transannular steric interactions of this type were not important if the phenyl rings assumed an orientation "parallel" to the C2- - -C4 vector ($\phi_1 = \phi_3 = 90°$). However, in this case steric interactions involving the ortho hydrogens and the methoxycarbonyl groups may come into play. These interactions might be expected to be particularly severe for **1** where both ester groups were exo. This would appear to explain why both phenyl groups of the exo–exo isomer, **1**, adopted a nearly "bisecting" conformation with $\phi_1 = 17°$ and $\phi_3 = 37°$. In contrast, the phenyl rings of the endo–endo isomer, **2**, had a more nearly "parallel" orientation with $\phi_1 = 69°$ and $\phi_3 = -85°$. For the exo–endo isomer, **3**, $\phi_1 = 56°$ and $\phi_3 = -60°$.

It should be noted that the steric interactions involving the ortho hydrogens were alleviated to an additional extent through another type of deviation from the model structure. When the phenyl carbon atoms C5 and C11 were in plane P1 and P2, respectively, the bond angles C3–C1–C5 and C1–C3–C11 can be represented by δ_1 and δ_3, respectively, and they were related to the folding angle τ by $\delta_{\text{calcd}} = 90 + (\tau/2)$. The calculated value for δ for the exo–exo isomer, **1**, was 135°. In fact, the observed values for **1** were $\delta_1 = 140.6°$ and $\delta_3 = 143.0°$, which showed that the phenyl groups splayed from P1 and P2 away from the two exo methoxycarbonyl groups and away from each other. Despite this splaying effect and the rotation of the phenyls toward a "bisecting" conformation, there was still a relatively short nonbonded steric interaction of 2.40 Å between the ortho hydrogen (H16) and the carbonyl oxygen (O1).[19]

By contrast, the more nearly "parallel" oriented phenyls of the endo–endo isomer, **2**, were bent out of P1 and P2 *toward* each other but again *away* from the two endo methoxycarbonyl groups ($\delta_1 = 130.2°$, $\delta_3 = 131.8°$, $\delta_{\text{calcd}} = 143.9°$). The shortest distances involving the aromatic ortho hydrogens were between H16 and H2 (2.34 Å) and H12 and H4 (2.39 Å).

In the mixed stereoisomer, **3**, there was no splaying of the phenyl groups from P1 and P2 ($\delta_1 = 140.0°$, $\delta_3 = 139.0°$, $\delta_{\text{calcd}} = 139.8°$). For this exo–endo isomer, the shortest nonbonded distances involving the aromatic ortho hydrogens are for H12–H4 (2.26 Å) and H6–H4 (2.32 Å).

The structures of **1**, **2**, and **3** are given in Figures 3, 4, and 5, respectively, while the experimental bonding parameters discussed above are given in Table VII. As can be readily noted from Table VII, the exo–exo isomer, **1**, is the most "puckered" or "nonplanar" bicyclo[1.1.0]butane derivative, while the endo–endo isomer, **2**, is the least "puckered" of this set of three compounds. As the "puckering" of the bicyclo[1.1.0]butane skeleton decreases, the C1–C3 bond length, *b*, increases. It is both experimentally and theoretically interesting that an *inward* displacement of the bridgehead substituents occurred despite the flattening of the bicyclo[1.1.0]butane skeleton of **2** ($\tau = 107.8°$, $\theta = 127.2°$).[20] This was consistent with earlier indications.[7-9] This implies that as the bicyclo[1.1.0]butane envelope opens the interflap angle,

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(19) There is no transannular phenyl–phenyl interaction shorter than 2.76 Å that occurs between H16 and H10.

(20) The bridgehead carbons, C1 and C3, are "pyramidal" in that all four atoms, to which each of these bridgehead atoms are bonded, can lie on one side of a plane passing through the bridgehead carbon.

Table VIII. RHF Optimized Geometry Parameters as a Function of X in the Relationship $\theta_{opt} + X$ = Interflap Angle

	X, deg						
	−20	−10	0	10	20	30	40
b, Å	1.433	1.440	1.460	1.473	1.491	1.521	1.562
c, Å	1.512	1.489	1.472	1.475	1.471	1.472	1.467
d, Å	2.023	2.122	2.203	2.306	2.375	2.428	2.442
θ, deg	98.9	108.9	118.9	128.9	138.9	148.9	158.9
δ, deg	141.7	138.9	134.4	132.7	129.4	126.8	124.6
α, deg	56.6	57.8	59.4	59.9	60.9	62.2	64.3
λ, deg	108.9	110.4	109.5	110.2	109.6	109.2	108.6
β, deg	61.7	61.1	60.3	60.0	59.6	58.9	57.8
η, deg	119.3	119.2	120.2	118.4	118.0	117.8	118.1
ω, deg	122.3	120.8	119.9	121.0	121.5	121.6	121.1
energy, kcal/mol	20.0	5.0	0.0	3.8	15.5	31.5	51.3
bond order of *b*	0.979	0.959	0.933	0.916	0.889	0.857	0.813

θ, increases and the substituents at C1 and C3 move progressively out of the planes P1 and P2 and toward each other. Whether this was a specific result of the substituents on **1**, **2**, and **3** or whether it represents a general property of "inverting" derivatives of bicyclo[1.1.0]butane was of significant concern. This interest was reflected in a detailed theoretical evaluation of the inversion process for the parent compound, bicyclo[1.1.0]butane (**4**).

Theoretical Studies

Our restricted Hartree–Fock (RHF) calculations are summarized in Table VIII. For values of X > 0° (values of $\theta > \theta_{opt}$[21]), the C1–C3 bond length, *b*, increased, while for X < 0°, *b* decreased as previously noted by Paddon-Row et al.[8] Our calculations show that δ decreased from the optimized value as X went from 0° (θ = 118.9°) to 40° (θ = 158.9°) and increased as X went from 0° to −20° (θ = 98.9°). The value of *b* varied little for X < 0°, while for X > 0° this bond length increased. This may be due to increased steric repulsions between the two methylene groups. As X increased, the increase in *b* was coupled to an increase in α. This increase in the C1–C2–C3 bond angle, α, was in turn coupled with a decrease in the H–C2–H bond angle, λ, as would be expected from similar relationships in simple strained monocyclic systems.[3,22]

The trends observed at the restricted Hartree–Fock level were in agreement with the experimental trends observed by us for **1**, **2**, and **3** and by others for constrained polycyclic systems.[10,11] This suggests that electronic effects play an important role in determining the structure of bicyclo[1.1.0]butane and the orientation of the bonds attached directly to this hydrocarbon skeleton and that the structure of the nucleus is little perturbed by crystal packing forces. As shown in Table VIII, the RHF energies relative to the optimized structure (defined at X = 0°) are much too large. It would appear that this error in energetics occurred because the RHF wave function failed to describe adequately the partial dissociation of the C1–C3 bond in the inversion process.

In order to better characterize the inversion process, our calculations were repeated at the generalized valence bond (GVB) level. The GVB results are shown in Table IX for X = −10–61.1°. This latter value corresponded to θ = 180°, which was the planar carbon skeleton. We have found that the planar structure is a two configurational state that cannot be adequately described at the RHF level, as would have been expected for such a diradical. As can be noted from a comparison of Tables VIII and IX, the value for *b* was significantly longer at the GVB level than at the RHF level. This was expected since the GVB wave function allowed the C1–C3 bond to properly dissociate while the RHF wave function did not. The values from the GVB calculations for δ clearly showed the same trend in the region X = −10–30° as was found at the RHF level and as was found experimentally. The other general trends found at the RHF level were reproduced at the GVB level with two exceptions. These were (1) the nonbonded C2- - -C4 distance, *d*, which showed a much smaller variation at the GVB level and reached a maximum for a significantly smaller value of X, and (2) at the GVB level, δ reached a minimum near X = 30° (θ = 148.9°) and then increased as θ approached 180°, whereas the RHF calculations showed a continual decrease in δ.

The geometry for the planar form of bicyclo[1.1.0]butane, where θ = 180°, was initially optimized in D_{2h} symmetry (see Table IX). However, the unusual variation of δ suggested that while the four carbon atoms were coplanar, the hydrogens at C1 and C3 may not lie in the plane of these carbons. In verification of this idea, an optimization of the H–C1–C3 angle for θ = 180° led to a value for δ of 147.2° and a structure with C_{2v} symmetry. The energy of this C_{2v} "planar" structure was almost 4 kcal/mol less than that of the D_{2h} structure.[23]

A useful approach to the analysis of the GVB results was to examine the bond order[25] of the C1–C3 bond that is given in Table IX. Our calculations indicated that the bond order decreased throughout the inversion process and, even though the difference was small, the optimum bond order for the C_{2v} planar structure was significantly greater than the bond order for the D_{2h} structure.

As noted above, an increase of approximately 4 kcal/mol was required to convert the C_{2v} structure into the D_{2h} structure. There are two reasons for this increase. The first is that, for the C_{2v} structure, there was somewhat more overlap (a higher bond order) for the C1–C3 bond. A second reason is that the H–C1–C2 and H–C1–C4 bond angles, which were 132.6° in the D_{2h} structure, were reduced to 124.7° in the C_{2v} structure. This alleviated some angle strain in the C_{2v} configuration. Overall, the energy of the planar structure was probably too low in comparison to the optimum structure for unperturbed bicyclo[1.1.0]butane since a minimum basis set would probably favor the planar form over the bent form.

In order to further investigate the inversion process for bicyclo[1.1.0]butane, a Linear Synchronous Transit path (LST)[26] from the optimum structure of **4** to the planar D_{2h} structure was constructed. A summary of the results is presented in Table X as a function of X. Since this was a synchronous path, δ was constrained to increase in a least-motion sense. As can be noted from the table, the energies increased and then decreased, which suggested the presence of an additional energy barrier between the ground state and the D_{2h} planar form when a least-motion path was followed. For a given value of X, the energies of the optimized structures, with the C1 and C3 bridgehead hydrogens rotated inward, were always lower than the LST structures with the hydrogens rotated outward. These results indicated that the inversion process for bicyclo[1.1.0]butane followed a non-least-motion path. The bridgehead hydrogens initially rotated inward and then had to switch their direction of motion before inversion could occur. Inversion occurred only after an additional barrier was surmounted to reach the D_{2h} planar form.

Analysis of the wave function for the planar form in terms of natural orbital occupancies and the overlap between the GVB orbitals[27] provided a useful insight into the electronic structure

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(21) The value of θ was determined by point-wise geometry optimization. The optimized value of θ compares well with the experimental value of 122.7° determined by Cox, Harmony, Nelson, and Wiberg in ref 12.

(22) Bartell, L. S.; Bonham, R. A. *J. Chem. Phys.* **1959**, *31*, 400. Kuchitsu, K. *Ibid.* **1966**, *44*, 906.

(23) A similar prediction of a small value for δ (119°) with a large value for θ (144°) has been reported[24] for 2,4-dimethylenebicyclo[1.1.0]butane. For this molecule as an approximately planar (θ = 176°) singlet, the calculated value for δ was 159° rather than 180°.[24]

(24) Feller, D.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1982**, *104*, 1216.

(25) We employ bond orders as defined by: Armstrong, D. R.; Perkins, P. G.; Stewart, J. P. *J. Chem. Soc., Dalton Trans.* **1973**, 838. Although these bond orders are not rigorously defined for open-shell wave functions, good agreement between the expected values and the bond orders has been found by us in other studies.

(26) Halgren, T. A.; Lipscomb, W. N. *Chem. Phys. Lett.* **1977**, *49*, 225.

of the transition state for the ring "flipping" of bicyclo[1.1.0]butane. For the planar D_{2h} structure, the natural orbital occupations were 1.12 and 0.88 for the two leading natural orbitals. These two orbitals closely resembled the canonical HOMO and LUMO. The value of the overlap between the GVB orbitals was 0.06. For a pure 1,3-diradical, the natural orbital occupations would be 1.00 for each orbital and the overlap between the GVB orbitals would be 0.00. Thus, a small amount of bonding character remained in the C1–C3 bond, *b*, in the D_{2h} planar form even though *b* was 2.03 Å. This implied that the D_{2h} planar structure was not completely diradical in nature.

It is interesting that for the D_{2h} structure, the dominant natural orbital had symmetric overlap (HOMO) that could be contrasted with the predictions of Paddon-Row et al.[8] For the C_{2v} planar structure, the overlap between the GVB orbitals increased to 0.09, and the occupancy of the HOMO increased to 1.18 and that of the LUMO decreased to 0.82.

The nature of the HOMO in a simple RHF-MO framework changed between X = −10° and X = −20°. At −10°, the HOMO was localized in the region of the C1–C3 bridging bond[28] and, as discussed previously, was composed predominantly of p character, being approximately 50% p–π and 50% p–σ as shown in Figure 6a. The LUMO corresponded to the antibonding component of this orbital. Thus, ionization (electron loss) was predicted to occur from the region of the C1–C3 bond, *b*, as per our earlier findings.[28]

At X = −20°, the HOMO changed character and was localized on the C1–C2 type bonds, *c*, as shown in Figure 6b. The orbital interactions between the orbitals of the bridgehead carbons and the orbitals of the bridging carbons (C2 and C4) led to positive overlap while the interactions between the orbitals on C1 and C3 introduced an enhanced antibonding state. Intriguingly, relative to our earlier work,[28] this study predicted that at X = −20° the C1–C2 bond should be ionized more readily than the C1–C3 bond. At X = −20°, the LUMO was still associated with the C1–C3 bond.

Discussion

Our calculations provide a detailed picture of the inversion process in bicyclo[1.1.0]butane. The most significant feature is that as the interflap angle (θ) increases to a value of 150°, the value of δ decreases. At the same time, the transannular distance between the bridgehead hydrogens also decreases. As θ increases beyond 150°, a reversal occurs and the value of δ increases until θ reaches 180°. However, δ does not reach the value of 180° required for a D_{2h} structure. As shown in Figure 7, when δ is plotted as a function of θ, the behavior of δ, up to $\theta \sim 125°$ is linear while a pronounced curvature in the plot of θ vs. δ is observed for $\theta > 125°$. The experimental values of δ are scattered about the theoretical curve. We wish to stress that the line predicted by Paddon-Row et al.[8] is very close to ours, but that their calculations only cover the linear portion of our curve. The deviation of the bridgehead hydrogens from the planes P1 and P2 (defined as Δ) can also be plotted vs. θ or, equivalently, vs. the interplane angle, τ. The plot of Δ vs. τ is shown in Figure 8. We find that Δ is essentially a linear function of τ up to a value of $\tau = 140°$ and follows a relationship of the form $\Delta = 0.937\tau - 88.4$. For $\tau > 150°$, the value of Δ decreases as τ is increasing. This interesting variation in δ and Δ correlates quite well with the nature of the bridgehead bond. The change in direction in δ occurred when the bond order was ~0.50. As the diradical nature of the bond between the bridgehead carbons increased beyond a value of 0.5, the dominant physical constraint on the process was no longer to maximize the bond overlap and to alleviate strain in angle δ but to alleviate angular strain in angles γ and ψ, since these were the crucial angles for the incipient diradical. The CH_3 radical is known to be planar[29] and all bond angles are 120°. While some deviation from the trigonal planar structure of the methyl radical may occur if a methyl group is substituted for hydrogen, this deviation is not expected to be large. When a carbon radical is placed in a four-membered ring, the C_2–C_1–C_4 internuclear angle (γ) will be significantly less than 120°, eg., ranging from $\gamma = 101°$ at X = 30° (50% radical character) to $\gamma = 94°$ at X = 61.1° (ca. 100% radical character). If the carbon radical becomes nonplanar, it can relieve some angular strain by reducing ψ. The value of ψ should remain as small as possible to relieve this strain. Further evidence that angular strain plays a role in these systems was seen by comparing ψ and δ. In the region 0° < X < 40°, the values of ψ and δ are comparable, which suggests that an equalization of angular strain is important.

Although the relative energetics of the phenyl and methoxycarbonyl derivatives have not been calculated, the calculations on the parent hydrocarbon and the orientations of the substituents from the crystal structure determinations provide some explanation of the changes in θ and γ for the substituted compounds. When we consider the structures of the substituted species as being deviations from an ideal structure represented as having all hydrogen substituents, we find that substitution of two large groups in the endo positions forces the flap angle to increase. This will lead to a decrease in δ. Since the exo substituents are small (i.e., H), the phenyl groups at the bridgehead have essentially a "parallel" orientation. Thus, the values of δ are comparable to those calculated for the parent hydrocarbon at the experimental value of θ for **2**, since there is very little steric interaction between the phenyl substituents.

Similarly, substitution of two methoxycarbonyl groups in the exo position forces the two phenyl groups away from a "parallel" orientation since there would be large steric interactions between the phenyls and the methoxycarbonyl groups. However, the phenyls cannot adopt a "bisecting" orientation since this would lead to large steric interactions between them. Thus, δ must increase in order to minimize this strain and to obtain a partially "bisecting" orientation of the phenyls. The increase in δ leads to a decrease in θ in accord with the predictions of the calculations. Since the endo substituents are hydrogens, the value of θ can and does decrease. In fact, δ can increase even more than predicted by the calculations in order to relieve this strain. Thus, the deviations from the hydrocarbon in the endo–endo and exo–exo isomers (**2** and **1**, respectively) are due to different steric interactions. Since the endo–endo isomer has a smaller deviation in θ from θ_{opt} than does the exo–exo isomer and since for small deviations from θ_{opt} less energy is required to increase θ than to decrease it, the endo–endo isomer should be lower in energy than the exo–exo isomer. This also follows from the deviations in δ, where the deviation in δ_{exp} from δ_{calc} is much larger for the exo–exo isomer than for the endo–endo isomer. The above reasoning helps to rationalize the experimental result of Woodward and Dalrymple which showed that the endo–endo isomer, **2**, was more stable than the exo–exo isomer, **1**.

The structure of the endo–exo isomer, **3**, appears to be regulated by a balance of steric interactions. A single substituent in the endo position should cause θ to be greater than θ_{opt}. However, an increase in θ results in a decrease in δ. This necessitates a strong interaction between the bridgehead phenyls and the exo methoxycarbonyl group. Since δ is increased over the value for δ_{calcd}, this steric interaction appears to be important. The presence of the endo substituent prevents θ from decreasing in order to increase

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(27) We define the GVB wave function as $\psi = {}^1/_2[(1 - \lambda^2)^{1/2} + \lambda]\bar{A}\cdot[(\text{core})^2(\bar{a}b + b\bar{a})]$ where $\bar{A}$ is the antisymmetrizer, $(\text{core})^2$ is the doubly occupied core orbitals, *a* and *b* are the GVB split-pair orbitals, and λ is a configurational mixing parameter. The value of the overlap S_{ab} is given by $S_{ab} = [(1 - \lambda^2)^{1/2} - \lambda]/[(1 - \lambda^2)^{1/2} + \lambda]$. S_{ab} provides a useful measure of the bonding between the split-pair orbitals and for a pure diradical. $\lambda = 1/2^{1/2}$, and $S_{ab} = 0$. One can also write the above wave function in terms of natural orbitals $\psi = (1 - \lambda^2)^{1/2}\bar{A}[(\text{core})^2a'\bar{a}'] - \lambda\bar{A}[(\text{core})^2b'\bar{b}']$ where $a'\bar{a}'$ and $b'\bar{b}'$ are the natural orbitals corresponding to *a* and *b*, the GVB split pair. The occupations (N_i) referred to in the text are those for the natural orbitals. For a pure radical $N_{a'} = N_{b'} = 1$.

(28) For leading references see: Gassman, P. G.; Mullins, M. J.; Richtsmeier, S.; Dixon, D. *J. Am. Chem. Soc.* **1979**, *101*, 5793. Pomerantz, M.; Abrahamson, E. W. *Ibid.* **1966**, *88*, 3970. Schulman, J. M.; Fisanick, G. J. *Ibid.* **1970**, *92*, 6653. Newton, M. D.; Schulman, J. M. *Ibid.* **1972**, *94*, 767, 773. Hehre, W. H.; Pople, J. A. *Ibid.* **1975**, *97*, 6941.

(29) Maryneck, D. S.; Dixon, D. A. *Proc. Natl. Acad. Sci. U.S.A.* **1977**, *74*, 410.

Table IX. GVB Optimized Geometric Parameters[c] for Different Values of X in the Relationship θ_{opt} + X = Interflap Angle

	X, deg									
	−10	0	10	20	30	40	50	55	61.1[a]	61.1[b]
b, Å	1.462	1.493	1.530	1.608	1.761	1.936	2.016	2.049		2.031
c, Å	1.489	1.481	1.476	1.474	1.480	1.495	1.500	1.502		1.499
d, Å	2.112	2.204	2.279	2.313	2.293	2.240	2.212	2.195		2.206
θ, deg	108.9	118.9	128.9	138.9	148.9	158.9	168.9	173.9		180
δ, deg	140.0	136.7	132.0	125.1	118.3	122.5	134.5	139.3	147.2	180
α, deg	60.6	60.5	62.4	66.1	73.0	80.7	84.4	86.0		85.3
λ, deg	110.4	111.0	110.1	109.9	109.1	108.6	107.4	102.7		106.8
β, deg	58.8	59.7	58.8	56.9	53.5	49.6	47.8	47.0		47.4
η, deg	119.0	118.9	118.3	117.0	117.1	116.0	116.4	115.9		116.0
ω, deg	120.6	119.7	120.4	120.5	118.5	116.8	115.6	118.4		116.0
ψ, deg	134.5	131.9	128.4	123.7	118.1	117.8	121.5	122.9	124.7	132.6
γ, deg	90.3	96.1	101.0	103.4	101.5	97.0	95.0	93.8	94.8	94.8
energy, kcal/mol	5.0	0.0	2.8	9.5	14.2	16.2	17.8	20.0	19.2	23.2[d]
bond order of b	0.90	0.87	0.82	0.73	0.52	0.25	0.10	0.06	0.04	0.03

[a] Positions of bridgehead hydrogens optimized. [b] Optimized in D_{2h} symmetry. [c] For a definition of parameters see text and Figure 1. [d] $\Delta H^{\ddagger}$ for the conversion of **1** to **2** has been reported to be 26 ± 2 kcal/mol.[4]

Table X. GVB Linear Synchronous Transit (LST) Path for the Inversion of Bicyclo[1.1.0]butane

path variable[a]	X, deg	b, Å	δ, deg	energy, kcal/mol	bond order of b
0.0	0	1.491	135.6	0.0	0.87
0.07	3.3	1.544	138.7	1.4	0.81
0.14	6.8	1.597	142.1	5.3	0.76
0.22	10.6	1.650	146.1	10.8	0.70
0.31	14.9	1.704	150.7	17.8	0.61
0.41	19.8	1.759	156.0	24.7	0.49
0.52	25.8	1.816	161.6	29.2	0.34
0.54	27.5	1.830	163.0	30.0	0.30
0.57	29.4	1.845	164.4	30.4	0.26
0.60	31.4	1.860	165.8	30.4	0.22
0.64	33.5	1.875	167.2	30.2	0.19
0.70	38.1	1.904	169.8	29.4	0.13
0.77	43.1	1.932	172.2	27.5	0.09
0.90	57.4	1.981	176.4	24.2	0.04
1.00	61.1	2.017	180.0	22.9	0.03

[a] The first path variable is the percentage change in going from the structure at X = 0° to X = 61.1° as defined in ref 26.

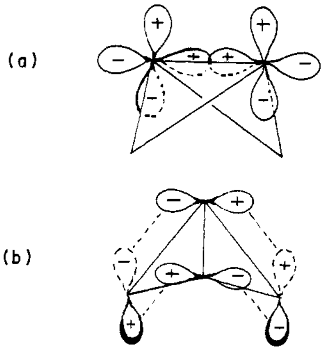

Figure 6. (a) Orbital interactions of the HOMO of bicyclo[1.1.0]butane with an interflap angle, θ, of 108.9°. (b) Orbital interactions of the HOMO of bicyclo[1.1.0]butane with an interflap angle, θ, of 98.9°.

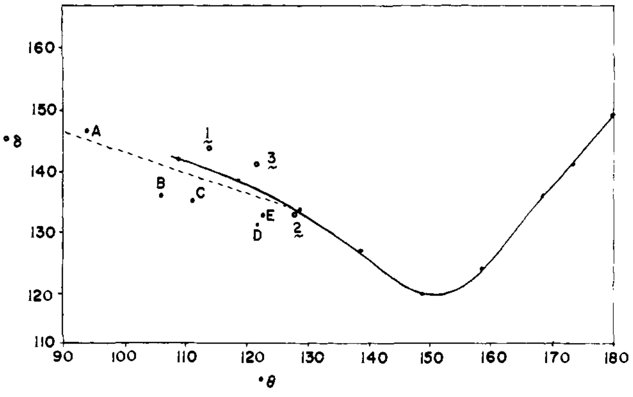

Figure 7. The variation of δ (angle H–C1–C3) as a function of θ (the interflap angle). The theoretical line of Paddon-Row et al.[8] is dashed. The solid line represents the GVB curve calculated in this work. The experimental points for **1**, **2**, and **3** from this work are indicated as open circles. Experimental points A, B, and C are from ref 10a. Point D is the experimental data for bicyclo[1.1.0]butane.[12] Point E is from: Kabuto, C.; Tatuoka, T.; Murata, I.; Kitahara, Y. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 669.

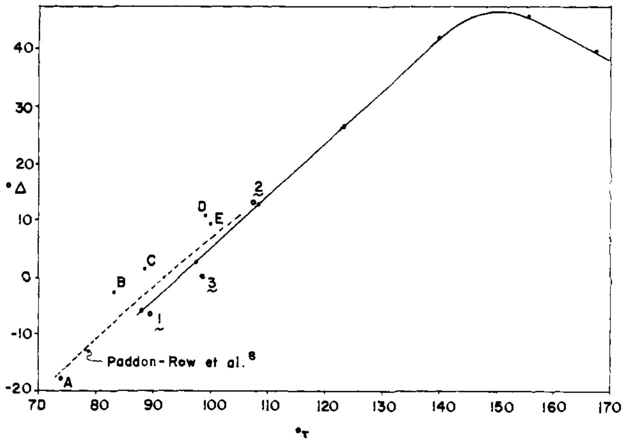

Figure 8. The variation of Δ (δ − δ(ideal)) as a function of τ (the folding angle) as calculated by GVB. The angle Δ corresponds to the deviation of the bridgehead substituent from plane P1 defined by C2, C1, and C4. This relationship as derived from the calculations of Paddon-Row et al.[8] is also included in this figure as the dashed curve. The experimental points for **1**, **2**, and **3** from this work are indicated as open circles. Experimental points A, B, and C are from ref 10a. Point D is the experimental data for bicyclo[1.1.0]butane.[12] Point E is from: Kabuto, C.; Tatuoka, T.; Murata, I.; Kitahara, Y. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 669.

δ. Although the experimental value for θ is near the optimum value for the parent hydrocarbon, we caution against employing only the energetic variations with θ to predict that the endo–exo isomer is the most stable. Indeed, the various steric interactions could be additive leading to the endo–exo isomer being the least stable.

Summary

In terms of an overview, we have shown that the observations of Woodward and Dalrymple, which provided the impetus for this study, were based on sound deductions. As a result of our experimental structural studies, it has become clear that the bicyclo[1.1.0]butane skeleton is amazingly flexible. Relatively little energy is required for an interflap angle (θ) variation of 20°. As a result of careful theoretical evaluation of varying the interflap angle, we were led to an investigation of the inversion process for bicyclo[1.1.0]butane. We found that this process involved a non-least-motion movement of the substituents on C1 and C3 of the hydrocarbon skeleton.

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Registry No. 1, 7577-40-4; **2**, 23201-79-8; **3**, 7577-41-5; **4**, 157-33-5.

Supplementary Material Available: Positional and thermal parameters and their estimated standard deviations and observed and calculated structure factors are provided for the X-ray structure determinations of **1**, **2**, and **3** (23 pages). Ordering information is given on any current masthead page.

Annulated Pyranosides. 4.[1a] Routes to Cyclohexano and Cyclopentano Pyranosides from Carbohydrate α-Enones[1b]

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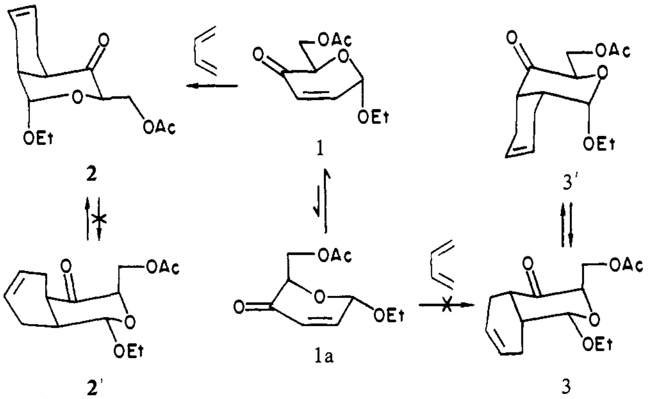
Abstract: Diels–Alder addition of butadiene to ethyl 6-*O*-acetyl-2,3-dideoxyhex-2-enopyranosid-4-ulose proceeds at low temperature in excellent yield when catalyzed by aluminum trichloride. Addition is exclusively from the β-face leading to the product having a 2,3-dideoxy α-D-*lyxo* configuration. The system is conformationally immobile, and reduction of the carbonyl group occurs from the α-face of the pyranoside ring (i.e., exo to the oxa-*cis*-decalin surface), giving a single alcohol, endo to the bicyclic system, which is so hindered that even benzylation required lengthy reaction times. Various attempts to contract the cyclohexenyl ring are described. Failure was met in all cases with the cyclohexenyl pyranosides. However, when the sugar ring was contracted first, the resulting cyclohexenyl furanose underwent cyclohexane to cyclopentane conversion via oxidative cleavage followed by a Dieckmann cyclization.

In a recent communication[5] we outlined a route to the enantiomers of chrysanthemumdicarboxylic acid in which the cyclopropyl moiety was mounted upon a pyranoside template. Because of their prevalence among natural products, cyclopentano and cyclohexano systems are of particular interest. Stork's early synthesis of prostaglandin[6] and recent alternative approaches to these important compounds by Ferrier[7] and Horton[8] indicate methodology for cyclopentanes from sugars, as do reports from Vasella's laboratory.[9] With regard to six-membered rings, routes utilizing dicarbonyl sugars have been developed by Kiely[10] and Ferrier.[11]

It is interesting to note that these[6-11] routes to carbocyclic systems utilize acyclic sugar derivatives, some by cyclization,[6,7,10,11] others by cycloaddition.[8,9] Thus the sugar moiety serves as an agent for "chirality transfer"[12] to the carbocycle. We have been concerned with the use of the carbohydrate ring system not only for "chirality transfer" but also as a device for eliciting highly stereocontrolled reactions. The role of the anomeric effect in producing a reliable, conformationally biased template,[13] well-known to carbohydrate chemists,[14] is now fully appreciated,[15,16] and we wish to take advantage of this powerful force. We have been investigating the preparation of "annulated sugars"[17,18] in

Scheme I



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(1) (a) For parts 1, 2, and 3 see ref 17, 5, and 18, respectively. (b) Taken in part from: Anderson, R. C.; Primeau, J. L. Ph.D. Theses, University of Waterloo, 1978 and 1982, respectively. For a preliminary account of this work see ref 17.

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(4) University of Maryland. Address correspondence to this author at Paul M. Gross Laboratory, Department of Chemistry, Duke University, Durham, NC 27706.

(5) Fitzsimmons, B. J.; Fraser-Reid, B. *J. Am. Chem. Soc.* **1979**, *101*, 6123.

(6) Stork, G.; Takahashi, T.; Kawamoto, T.; Suzaki, T. *J. Am. Chem. Soc.* **1978**, *100*, 8272. Stork, G.; Takahashi, T. *Ibid.* **1977**, *99*, 1275. Stork, G.; Raucher, S. *Ibid.* **1976**, *98*, 1583.

(7) Ferrier, R. J.; Prasit, P. *J. Chem. Soc., Chem. Commun.* **1981**, 983.

(8) Horton, D.; Machinami, T. *Ibid.* **1981**, 88.

(9) Vasella, A. *Helv. Chim. Acta* **1977**, *60*, 1273. Von Bruno, B.; Vasella, A. *Ibid.* **1979**, *62*, 1990.

(10) Kiely, D. E.; Cantrell, C. E. *Carbohydr. Res.* **1972**, *23*, 155.

(11) Blattner, R.; Ferrier, R. J., *J. Chem. Soc., Perkin Trans. 1* **1980**, *1523*, 1528. Blattner, R.; Ferrier, R. J.; Prasct, P., *J. Chem. Soc., Chem. Commun.* **1980**, 944.

(12) Joullie, M. M.; Wang, P. C.; Semple, J. E. *J. Am. Chem. Soc.* **1980**, *102*, 887.

(13) Lemieux, R. U.; Koto, S. *Tetrahedron* **1974**, *30*, 1933.

(14) Szarek, W. A.; Horton, D. *ACS Symp. Ser.* **1979**, *No. 87*.

(15) Deslongchamps, P. *Tetrahedron* **1975**, *31*, 2463.

(16) Wolfe, S.; Rauk, R.; Tel, L. M.; Csizmadia, I. G. *J. Chem. Soc. B* **1971**, 136. Guibe, L.; Auge, J.; David, S.; Eisenstein, O. *J. Chem. Phys.* **1973**, *58*, 5579.

0002-7863/83/1505-5874$01.50/0