example, the shifts may be compared with those for the vinyl protons in cyclohexa-1,3-diene (τ 4.21) and *o*-xylene (τ 3.00), both in dilute $CDCl_3$ solution.

Conclusion

In the introductory statement, a survey of the evidence for strain in the benzocycloalkenes was given, and it was seen that there was little to suggest a partial loss of aromaticity in these compounds. The work in this paper has presented the first systematic examination of the proton-proton coupling constants between the aromatic protons in the strained benzocycloalkenes and a number of related molecules. It is found that the *ortho* couplings ($^3J_{HH}$) are insensitive to the strain, whereas $^4J_{HH}$ shows a significant decrease, and $^5J_{HH}$ a significant increase with strain. It should be emphasized that lack of thermochemical data means that only a qualitative estimate of strain energy can be made. The changes observed in $^4J_{HH}$ and $^5J_{HH}$ are in contrast to the insensitivity to strain of many other physical properties of these molecules.

A satisfactory qualitative explanation of these changes in the couplings may be given on the basis of empirical arguments which take into account the bond length, bond angle, and electronegativity changes thought to occur in these strained molecules. Many previous studies on "bond fixation" do not seem to have stressed enough the possible interplay of these factors. The results from an extended Hückel molecular orbital theory have also been presented in an attempt to describe the observed changes of these couplings on a reasonable theoretical basis. In view of the trends found for $^4J_{HH}$ and $^5J_{HH}$ in the present work, it would be of great interest to examine the ring-proton coupling constants in other strained aromatic compounds, for example, the cyclophanes.[75]

Before any more sophisticated theoretical treatment of these strained benzocycloalkenes is undertaken, it would seem necessary to obtain the molecular geometries, for example by X-ray or electron diffraction techniques. These values would also serve as a yardstick against which to test the success of geometries predicted using the method of Coulson and Longuet-Higgins,[6] or more recent theories.[76]

Acknowledgments. We thank Dr. H. Günther (Cologne, West Germany) for supplying results prior to publication, and both him and Dr. R. D. Rieke for helpful discussion. Professor E. Vogel (Cologne, West Germany) is most gratefully thanked for the generous sample of benzocyclopropene and for his interest. We thank Mr. J. H. Prestegard, Department of Chemistry, Caltech, for assistance in obtaining the 220-MHz spectra.

(75) For a review of the properties of these molecules, see: B. H. Smith, "Bridged Aromatic Compounds," Academic Press, New York, N. Y., 1964.

(76) See N. L. Allinger, J. A. Hirsch, M. A. Miller, I. J. Tyminski, and F. A. Van-Catledge, *J. Amer. Chem. Soc.*, 90, 1199 (1968), and references therein.

The Molecular Structure of Bicyclo[1.1.1]pentane

Joseph F. Chiang and S. H. Bauer

Contribution from the State University College, Oneonta, New York 13820, and the Department of Chemistry, Cornell University, Ithaca, New York 14850.

Received July 17, 1969

Abstract: This article reports on a molecular structure investigation of bicyclo[1.1.1]pentane by electron diffraction in the vapor phase. The data support a D_{3h} conformation, with dihedral angles of the cyclobutane rings fixed at 120°. The "best" structural parameters were obtained by applying a least-squares analysis to the experimental molecular intensities. These are: $C\text{–}C = 1.545 \pm 0.006$ Å, $\langle C\text{–}H\rangle_{av} = 1.100 \pm 0.010$ Å, $\angle C_1C_2C_3 = 73.3 \pm 1.0°$, $\angle HCH = 103.9 \pm 5.0°$. The separation between the bridgehead carbon atoms is 1.845 Å, the shortest nonbonded $C \cdots C$ distances on record, in complete agreement with the value found by X-ray diffraction for the 2-hydroxy-2-phenyl disubstituted derivative.

The structure of bicyclo[1.1.1]pentane presents interesting features of strained, fused four-membered ring systems. The dihedral angle for the cyclobutane rings is restricted to 120° by molecular symmetry. It appears evident that nonbonded carbon-carbon interactions are strong in this molecule. The present measurements of its molecular geometry in the gas phase by electron diffraction provide quantitative parameters for a theoretical treatment of this unusual structure.

Experimental Section

A purified sample of bicyclo[1.1.1]pentane was supplied by Dr. F. Uno and Professor J. Meinwald of the Department of Chemistry, Cornell University. Sectored electron diffraction patterns were taken with our new apparatus using a 70-kV electron beam, at 129- and 262-mm nozzle-to-plate distances. The sample was kept at 0° during the exposures. MgO patterns were recorded concurrently to establish the (λ L) scale factor. The diffraction patterns were microphotometered with a double beam Jarrell-Ash microdensitometer interfaced with a digital recorder. The procedure for data reduction and structure analysis has been described in several previous publications.[1]

Analysis and Results

The total experimental intensity curves for the two sets of data, along with the refined background, are plotted in Figure 1.[2] The reduced experimental $qM(q)$

---

(1) (a) J. L. Hencher and S. H. Bauer, *J. Amer. Chem. Soc.*, 89, 5527 (1967); (b) W. Harshbarger, G. Lee, R. F. Porter, and S. H. Bauer, *Inorg. Chem.*, 8, 1683 (1969); (c) R. L. Hilderbrandt and S. H. Bauer, *J. Mol. Structure*, 3, 825 (1969).

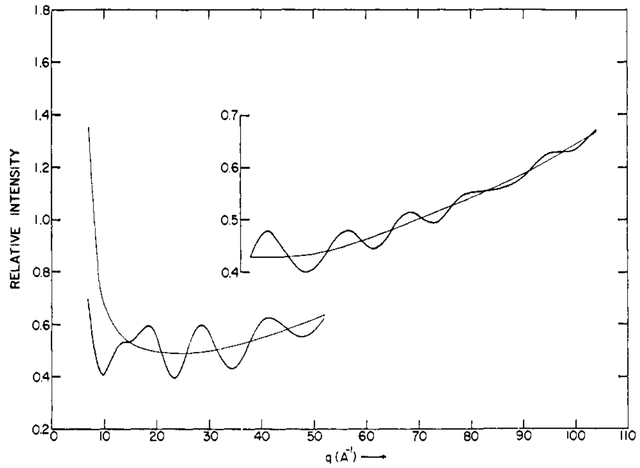

Figure 1. Relative intensities as a function of diffraction angle [$q = (40/\lambda) \sin \theta/2$] for long and short sample-plate distances.

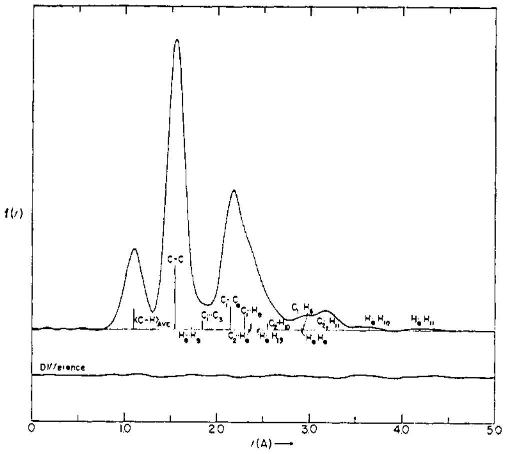

Figure 3. The experimental radial distribution curve and the difference between that and the curve calculated for the final model.

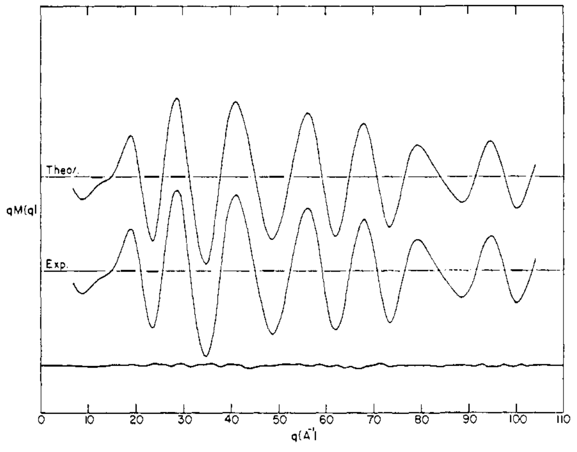

Figure 2. Comparison of the reduced experimental molecular scattering curve with that calculated for the final model; the lower jagged line is a plot of their difference.

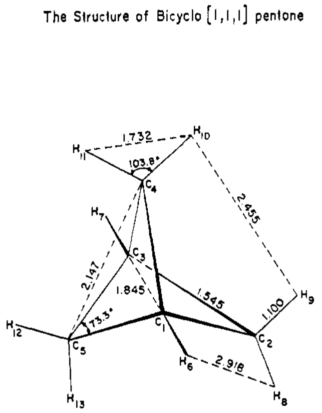

Figure 4. The structure of bicyclo[1.1.1]pentane.

curve and the corresponding theoretical molecular intensity curves for the final best model are shown in Figure 2. The refined experimental radial distribution curve is displayed in Figure 3, wherein the lower oscillating curve is the difference between this experimental function and the radial distribution calculated for the best model. D_{3h} symmetry was assumed for bicyclo[1.1.1]pentane in the calculation of its geometrical parameters, but departures from this symmetry were briefly tested, as discussed below. In the D_{3h} models the threefold rotational axis coincides with $H_6C_1C_3H_7$ and is perpendicular to the xy plane of $C_2C_4C_5$. In model A all the H atoms were located in the xy plane, in model B H_8, H_{10}, and H_{12} were placed above the xy plane with H_9, H_{11}, and H_{13} an equal distance below the plane. In the least-squares analysis model B *converged to model A* after 10 cycles.[3]

The following geometrical parameters were inserted in the calculation of the molecular geometry: C–C, $\angle C_1C_2C_3$, C–H$_{av}$, and $\angle$HCH. A least-squares analysis was applied to the experimental intensities. The calculation in which the geometrical parameters and the root-mean-square amplitudes l_{12}, l_{24} were allowed to vary (except that for C–H which was constrained) converged after 10 cycles. The average C–H distance can also be estimated from the radial distribution curve. The interatomic distances and l_{ij}'s which gave the smallest residuals and errors in the least-squares analysis,

Table I. Structural Parameters for Bicyclo[1.1.1]pentane

	r_{ij} (Å)	l_{ij} (Å)
C_1–C_2	1.545 ± 0.006	0.060 ± 0.006
⟨C–H⟩$_{av}$	1.100 ± 0.010	0.078[a]
$\angle C_1C_2C_3$	73.3° ± 1.0°	
$\angle$HCH	103.9° ± 5.0°	
	Calculated nonbonded distances	
$C_1 \cdots C_3$	1.845	0.160[a]
$C_2 \cdots C_4$	2.147	0.053 ± 0.004
$C_1 \cdots H_7$	2.945	0.100[a]
$C_1 \cdots H_8$	2.298	0.085[a]
$C_2 \cdots H_6$	2.372	0.090[a]
$C_2 \cdots H_{10}$	2.546	0.110[a]
$C_2 \cdots H_{11}$	3.194	0.090[a]

[a] These l_{ij}'s were assigned reasonable values and were constrained during the execution of the least-squares program.

(2) A listing of intensities supplementary to this article has been deposited as Document No. NAPS—00679 with the ASIS National Auxiliary Publication Service, c/o CCM Information Corp., 909 3rd Ave., New York, N. Y. 10022. A copy may be secured by citing the document number and by remitting $1.00 for microfiche or $3.00 for photocopies. Advance payment is required. Make checks or money orders payable to: ASIS-NAPS.

(3) This is not consistent with the model used by S. J. Cyvin, *et al.* (*Chem. Phys. Lett.*, **2**, 556 (1968)), in their calculations of mean-square amplitudes for this molecule; they assumed D_3 symmetry.

Table II. Error Matrix[a]

	C_1–C_2	C–H	$\angle C_1C_2C_3$	$\angle$HCH	l_{12}	l_{24}
C_1–C_2	0.0014					
C–H	−0.0009	0.0030				
$\angle C_1C_2C_3$	0.0027	−0.0132	0.3200			
$\angle$HCH	0.0043	0.0181	0.0851	1.1000		
l_{12}	0.0001	0.0007	0.0017	−0.0038	0.0014	
l_{24}	0.0002	−0.0021	0.0019	0.0050	0.0003	0.0011

[a] The equation for calculating these matrix elements is given in ref 1a. Distances are in ångström units; angles are in degrees.

Table III. Comparison of Bicyclo[1.1.1]pentane with Compounds Containing a Cyclobutane Ring

Compound	C–C (Å)	Angle (deg)	Ref
Bicyclo[1.1.1]pentane	1.545 ± 0.006	120	This study, ED
Cyclobutane	1.548 ± 0.003		ED[a]
Cyclobutane		145	Nmr[b]
Cyclobutane		147	Ir[c]
Octafluorocyclobutane	1.564 ± 0.003	170	ED[d]
Octachlorocyclobutane	1.575 ± 0.030	160	X-ray[e]
Octachlorocyclobutane	1.590 (av)	158	X-ray[f]
Tricyclo[3.3.0.0^{2,6}]octane	1.558 ± 0.003	126.7	ED[g]
Perfluorotricyclo[3.3.0.0^{2,6}]octane	1.48 (av)	120	X-ray[h]
Bicyclo[1.1.0]butane	1.498 ± 0.003	121.7	MW[i]
Bicyclo[2.1.1]hexane	1.547	129.5	ED[j]
Bicyclo[2.1.1]hexene	1.543	116.5	ED[k]
Bicyclo[3.1.1]heptane	1.553 ± 0.009	137	ED[l]
Cyclobutyl chloride	1.537 (av)	160	MW[m]
Bromocyclobutane	1.544 ± 0.003	151	MW[n]
Biscyclobutyl	1.548 ± 0.004	147	ED[o]
trans-1,3-Dibromocyclobutane	1.562 ± 0.006	148	ED[p]
trans-1,3-Chlorobromocyclobutane	1.551 ± 0.003	147	ED[p]
cis-1,3-Dibromocyclobutane	1.556 ± 0.007	147	ED[p]
cis-1,3-Chlorobromocyclobutane	1.549 ± 0.002	147	ED[p]
Urethan derivative of 2-hydroxy-2-phenylbicyclo[1.1.1]pentane	1.543 (av)	120	X-ray[q]

[a] Reference 6. [b] S. Meiboom and L. C. Snyder, *J. Amer. Chem. Soc.*, **89**, 1038 (1967). [c] D. A. Dows and Nathan Rich, *J. Chem. Phys.*, **47**, 333 (1967). [d] C. H. Chang and S. H. Bauer, unpublished. [e] T. N. Margulis, *Acta Crystallogr.*, **19**, 857 (1965). [f] T. B. Owen and J. L. Hoard, *ibid.*, **4**, 172 (1951). [g] Joseph F. Chiang and S. H. Bauer, *Trans. Faraday Soc.*, **64**, 2247 (1968). [h] I. L. Karle, J. Karle, T. B. Owen, and J. L. Hoard, *Acta Crystallogr.*, **18**, 345 (1965). [i] K. W. Cox, M. D. Harmony, G. Nelson, and K. B. Wiberg, *J. Chem. Phys.*, **50**, 1976 (1968). [j] Reference 8. [k] Reference 9. [l] G. Dallinga and L. H. Toneman, *Rec. Trav. Chim. Pays-Bas*, **88**, 185 (1969). [m] H. Kim and W. D. Gwinn, *J. Chem. Phys.*, **44**, 865 (1966). [n] W. G. Rothchild and B. P. Dailey, *ibid.*, **36**, 293 (1962). [o] Reference 7. [p] A. Almenningen, O. Bastiansen, and L. Walloe, *Select. Top. Struct. Chem.*, 91 (1967). [q] Reference 4.

along with several calculated nonbonded distances, are listed in Table I. The assigned error limits are three times the standard deviations; these are in excess of the estimated errors inherent in the sample-plate–voltage calibration, etc. The error matrix is reproduced in Table II; here the diagonal elements are the standard deviations for the corresponding parameters while the off-diagonal elements measure the correlation between parameters. No appreciable correlations exist for any pairs of parameters except the bond angles $\angle C_1C_2C_3$ with $\angle$HCH.

In the radial distribution curve, the first peak at 1.100 Å is due to the average-bonded C–H distances. The second peak at 1.545 Å is the bonded C–C scattering. The third peak is a superposition of some nonbonded C–C and C–H distances: $C_1 \cdots C_3$ = 1.845Å, $C_2 \cdots C_4$ = 2.147 Å, $C_1 \cdots H_8$ = 2.298 Å, $C_2 \cdots H_6$ = 2.372 Å, and $C_2 \cdots H_{10}$ = 2.546 Å. The last peak is due to the nonbonded C–H and H–H distances: $C_1 \cdots H_7$ = 2.945 Å, $C_2 \cdots H_{11}$ = 3.194 Å, etc. The locations of these distances are indicated by vertical lines along the axis in Figure 3, where the height of each is proportional to the quantity $C_{ij} = n_{ij}Z_iZ_j/r_{ij}$; n_{ij} is the number of atom pairs separated by the corresponding distances, r_{ij}, between atoms of atomic numbers Z_i and Z_j. The structure of bicyclo[1.1.1]pentane is shown in Figure 4.

Discussion

The structure of bicyclo[1.1.1]pentane presents a variety of interesting structural features. The interatomic distances and bond angles derived in this study in the vapor phase for the parent compound agree remarkably well with those found in the substituted derivative, 2-hydroxy-2-phenyl, bicyclo[1.1.1]pentane, investigated in the solid phase by X-ray diffraction (see Table III).[4] Further, the gas-phase ir spectrum indicates that the molecule is a symmetrical top. This conclusion is supported by the D_{3h} symmetry based on the electron-diffraction data. Nmr spectra[5] show that two different types of hydrogens are present, but model B with H_8, H_{10}, and H_{12} above the *xy* plane and H_9, H_{11}, and U_{13} below the plane could not be excluded. This investigation eliminates this possibility.

Whereas the C–C bond length agrees with those in cyclobutane,[6] biscyclobutyl,[7] bicyclo[2.1.1]hexane,[8] bicy-

---

(4) A. Padwa, E. Shefter, and E. Alexander, *J. Amer. Chem. Soc.*, **90**, 3717 (1968).

(5) K. B. Wiberg, G. M. Lampman, R. P. Ciula, D. S. Connor, P. Shertler, and J. Lavanish, *Tetrahedron*, **21**, 2749 (1965).

(6) A. Almenningen and O. Bastiansen, *Acta Chem. Scand.*, **15**, 711 (1961).

(7) A. DeMeijere, *ibid.*, 20, 1093 (1965).

(8) G. Dallinga and L. H. Toneman, *Rec. Trav. Chim. Pays-Bas*, **86**, 171 (1967).

clo[2.1.1]hexene,[9] and various other compounds containing cyclobutane ring, the C···C distance between the bridgehead atoms is the shortest nonbonded distance on record. If C_1 and C_3 are assumed to be nearly sp^2 hybridized, the almost p_z orbital of C_1 can participate in bonding with H_6, while its back lobe can overlap with the p_z from C_3. This type of hybridization at the bridgehead carbons does account for the large long-range proton spin–spin coupling constant (J_{C-H} = 18 cps) reported by Wiberg, *et al.*[5] This assumption is also supported by the product distribution found in the chlorination of bicyclo[1.1.1]pentane with *t*-butyl hypochlorite. This reaction produces 45% of 1-chlorobicyclo[1.1.1]pentane[5] and only 2% of 2-chlorobicyclo-[1.1.1]pentane, while the rest is the unreacted compound. This contrasts with bicyclo[2.2.1]heptane which is inert to 1 substitution.[10] The unexpectedly small ∠CCC at the methylenes is thus rationalized. A comparison of the environment at the bridgehead carbons in bicyclo[1.1.1]pentane, bicyclo[2.1.1]hexane, and bicyclo[2.2.1]heptane is postponed until the structure of bicyclo[2.1.1] has been redetermined.

The nonbonded $H_9 \cdots H_{10}$ distance is 2.45 Å, which is approximately twice the van der Waals radius of hydrogen atoms. This separation is consistent with the coplanarity of the H atoms with the methylene carbons, since no significant stabilization would be achieved by an out-of-plane distortion. The surprising feature is the small ∠HCH (104°). Clearly, the hybridization around the methylene carbons is not well approximated by an sp^3 combination. Perhaps the simplest description is to assume that the lobes of their relatively unhybridized p orbitals extend toward the bridgehead carbons and utilize principally the s orbitals for bonding with the hydrogen atoms. The results of an SCF-MO calculation of overlap populations and comments on this structure will shortly be submitted for publication by J. F. C.

Acknowledgments. The authors thank Mr. R. Hilderbrandt for taking the electron-diffraction photographs, and Dr. F. Uno and Professor J. Meinwald for the sample. We are grateful to Mr. J. Higgins of the Computer Center at SUNY, Binghamton, for various help during the analysis and State University College at Oneonta for furnishing the computer time.

Appendix A. Coordinates of Bicyclo[1.1.1]pentane[a]

	x	*y*	*z*
C_1	0	0	0.9222
C_2	1.2395	0	0
C_3	0	0	−0.9222
C_4	−0.6198	1.0734	0
C_5	−0.6198	−1.0734	0
H_6	0	0	2.0222
H_7	0	0	−2.0222
H_8	1.9175	−0.8662	0
H_9	1.9175	0.8662	0
H_{10}	−0.2086	2.0937	0
H_{11}	−1.7089	1.2275	0
H_{12}	−1.7089	−1.2275	0
H_{13}	−0.2086	−2.0937	0

[a] For numbering system, see Figure 4.

---

(9) Joseph F. Chiang and S. H. Bauer, to be published.

(10) E. C. Kooyman and G. V. Vegter, *Tetrahedron*, **4**, 382 (1958).

1-Methylbicyclo[3.1.1]heptan-6-one and Related Substances

Ernest Wenkert, Peter Bakuzis, Ronald J. Baumgarten, David Doddrell,
P. W. Jeffs, Curtis L. Leicht, Richard A. Mueller, and A. Yoshikoshi

Contribution from the Department of Chemistry, Indiana University,
Bloomington, Indiana 47401. *Received July 17, 1969*

Abstract: Base-induced conversions of 2-methyl-2-dichloromethylcyclohexanones to derivatives of the title compound and elucidation of their stereochemistry are discussed. Benzene solvent shifts of proton magnetic resonance spectra of haloolefins and their stereochemically diagnostic value are introduced. Syntheses of sesquiterpene models based on the bicyclo[3.1.1]heptane system are portrayed.

The polyfunctionality of alkyldichloromethylcyclohexadienones, products of alkali-induced interaction of alkylphenols with chloroform, makes these substances attractive starting materials for the synthesis of complex systems but necessitates prior investigations of their general chemical behavior. Such studies recently led to the discovery of facile transformations of 4-methyl-4-dichloromethyl-2,5-cyclohexadienone into polyfunctional bicyclo[3.3.1]nonanes and *cis*-decalins[1] and to the exploitation of the benz analog in the synthesis of tricarbocyclic diterpenes.[2] As further expansion of this fruitful area of research the chemical conduct of 6-methyl-6-dichloromethyl-2,4-cyclohexadienone (**1a**), a product of the Reimer–Tiemann reaction of *o*-cresol,[3] was examined.

Standard hydrogenation of **1a** has yielded 2-methyl-2-dichloromethylcyclohexanone (**2a**).[4] Controlled palladium-catalyzed hydrogenation and cessation of the reaction after a *ca.* 1-mole uptake of hydrogen yielded preponderantly the conjugated ketone **3a** and some of its isomer **4**. With time or on sulfuric acid treatment

---

(1) E. Wenkert, F. Haviv, and A. Zeitlin, *J. Am. Chem. Soc.*, **91**, 2299 (1969).

(2) (a) E. Wenkert and T. E. Stevens, *ibid.*, **78**, 5627 (1956); (b) E. Wenkert, A. Afonso, J. B-son Bredenberg, C. Kaneko, and A. Tahara, *ibid.*, **86**, 2038 (1964).

(3) K. Auwers and F. Winternitz, *Ber.*, **35**, 465 (1902); K. Auwers and G. Keil, *ibid.*, **35**, 4207 (1902).

(4) K. von Auwers and E. Lange, *Ann.*, **401**, 317 (1913).

Wenkert, et al. / *1-Methylbicyclo[3.3.1]heptan-6-one*