efficiently from triplet fluorenone.[41,42] Similar phenomena have been reported for pyrochlorophyll-sensitized photoreduction of nitro compounds in ethanol.[32,43] The fact that exchange of acceptor occurs within the triplet exciplex lifetime suggests that the triplet may be longer lived with perhaps considerable electron localization on the acceptor. Presumably the triplet exciplex comes very close to being an ion pair.

The differences between 4-nitrostilbene and 4,4'-dinitrostilbene as acceptors can be attributed to the greater electron affinity of the latter compound. The k_q values indicate that 4,4'-dinitrostilbene forms both singlet and triplet exciplexes faster than 4-nitrostilbene. The larger α values for the triplet exciplex suggest greater electron localization on the acceptor in the 4,4'-dinitrostilbene complexes.'

The differences in reactivity between the various donors are not readily explainable. The failure of tetracene and free base etioporphyrin to form triplet exciplexes is a little surprising. Tetracene has a low ionization potential (6.95 eV)[44] and its excited singlet is clearly more reactive as a donor than the excited singlet of zinc etioporphyrin (Table I). However the triplet energy of tetracene (29.3 kcal/mol)[45,46] is somewhat lower than the *ca.* 40 kcal/mol triplets of the porphyrins. In forming ground state charge-transfer complexes with trinitrobenzene, free-base tetraphenyl-

porphine is much more reactive than the zinc complex.[20] It is tempting to suggest that even though excitation and fluorescence clearly involve π,π^* states of the porphyrin, the metal plays the dominant role in exciplex formation. The effect of pyridine on reactivity of zinc and magnesium porphyrins is even more surprising. Both porphyrin pyridinates form triplet exciplexes with lower k_q^t values than in the absence of pyridine. The drastic reduction in k_q^t for zinc etioporphyrin pyridinate is much too great to be explained as a steric effect since the porphyrin is complexed on only one side. The lowering of k_q^t for magnesium etioporphyrin I pyridinate is less dramatic and it may or may not be related to steric factors or geometry of the magnesium. It is most surprising that pyridine enhances catalysis of acceptor isomerization by zinc but retards the same in the case of magnesium. Here again, exciplex lifetime may be a contributing factor. However, the more than tenfold increase in α, the fraction of exciplexes decaying with acceptor isomerization, indicates that pyridine specifically enhances isomerization. Participation of pyridine by interaction through d orbitals of the zinc may be a possibility, but no simple mechanism can be advanced at this time.

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Molecular Structure of Bicyclo[2.1.0]pentane

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Abstract: The molecular structure of bicyclo[2.1.0]pentane has been determined from electron diffraction studies of the vapor. The cyclobutane ring is planar and the interatomic distances are: $C_1-C_4 = 1.439 \pm 0.015$, $C_2-C_3 = 1.622 \pm 0.016$, $C_1-C_2 = 1.543 \pm 0.011$, $C_1-C_5 = 1.521 \pm 0.011$, and $C-H_{av} = 1.121 \pm 0.009$ Å. The dihedral angle between the two rings is $109.4 \pm 0.4°$ and the average H–C–H angle is $108.8 \pm 3.6°$. The salient features of the structure are the planar cyclobutane ring, the remarkably short distance, 1.439 Å, for the reactive zero-membered bridge bond, and the long 1.622-Å carbon–carbon bond length opposite the short bond in the cyclobutane ring.

T he conformation of a four-membered ring can be puckered or planar. Results of structural studies on many compounds related to cyclobutane have been tabulated by Adman and Margulis.[2] Prior to this study only puckered equilibrium configurations have been observed in free molecules of cyclobutane and derivatives containing neither cyclic nor exocyclic double

bonds.[3] In the solid state, some of these molecules have planar rings.[4] It appears likely, however, that the planar conformations are due to a dominance of crystal packing forces over intramolecular forces. On the other hand, four-membered ring compounds containing cyclic or exocyclic double bonds have planar

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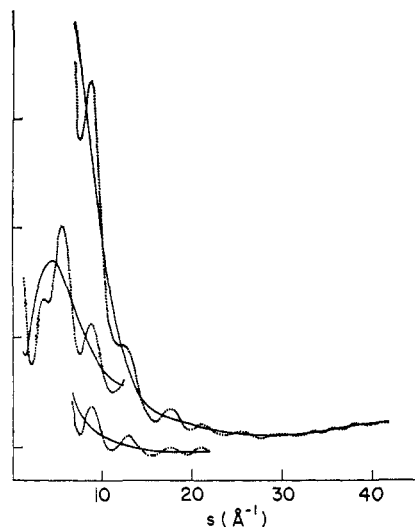(4) T. N. Margulis, *Chem. Commun.*, 215 (1969).

Figure 1. The observed intensities ($\cdots$) and background curves for the apparatus configurations 262 mm and 60 keV (upper), 130 mm and 25 keV (middle), and 130 mm and 60 keV (lower).
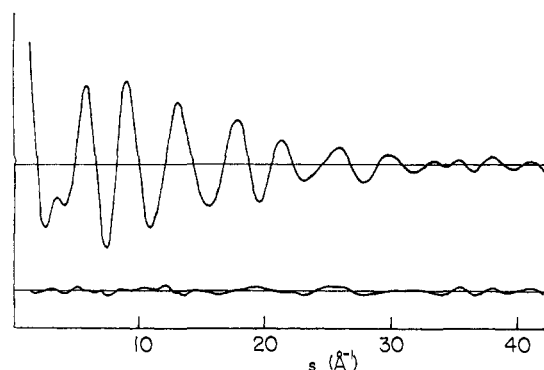

Figure 2. The "experimental" molecular intensity curve (upper), and the difference between it and the theoretical intensity calculated from the best model (lower).

equilibrium configurations, e.g., cyclobutene[5] and cyclobutanone.[6]

The C_1–C_4 bond in bicyclo[2.1.0]pentane has a strain energy of 47.4 kcal/mol.[7] This highly strained bond is also highly reactive. One especially interesting reaction is the facile cycloaddition of acetylenes or olefins across the bond.[8] Gassman and coworkers have studied this reaction extensively and determined that the reaction mechanism involves attack of the strained bond from below the flap of the envelope-shaped bicyclo[2.1.0]pentane molecule.[9]

An electron diffraction study of the structure of bicyclo[2.1.0]pentane was carried out to investigate the planarity of the four-membered ring and determine the structural parameters of this highly strained compound.

Experimental Section

The sample was obtained from Dr. John Chesick, then of Yale University. The purity of the sample was tested by vapor phase

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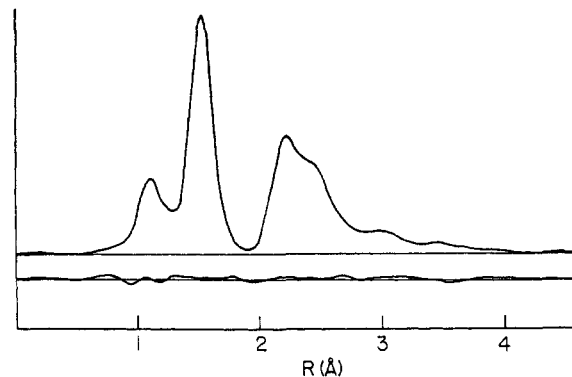(9) P. G. Gassman, K. T. Mansfield, and T. J. Murphy, *ibid.*, **90**, 4746 (1968).

Figure 3. The observed radial distribution curve (upper) with a damping constant of 0.001, and the difference between it and the radial distribution curve calculated from the best model (lower).

chromatography on a 6-ft 15–20% diisodecyl phthalate column. The elution time was 17 min. No other peaks before or 10 min after the sample peak were observed even with the amplifier set at a sensitivity 100 times greater than that used for the C_5H_8 peak. The mass spectrum was consistent with a compound of formula C_5H_8. The sample was used without further purification.

Electron diffraction patterns were obtained from the new electron diffraction apparatus at Cornell University.[10] Photographs covering three scattering regions were obtained using 25- and 60-keV beams at a nozzle-plate distance of 262 mm and a 60-keV beam with a 130-mm distance. The scattering regions included s = 1.25–12.50, 5.0–22.00, and 7.00–42.00 Å^{-1}, respectively. Calibration photographs of MgO were taken at each experimental configuration. The plates were photometered and the optical densities read at 0.25 s unit intervals were converted to the intensities shown in Figure 1. Backgrounds were drawn for each intensity curve and an "experimental" intensity function (see Figure 2) was calculated according to the following expression.

$$sM_{exp}(s) = s(I/B - 1)\sum_i \{[(Z_i - F_i)^2 + S_i]/$$

$$(Z_C - F_C)^2\}$$

I is the observed intensity, B is the background, and Z_i, F_i,[11] and S_i[12] are the atomic number, form factor, and inelastic scattering factor, respectively, for atom i. The larger angle data sets were scaled to agree with the amplitudes of the small angle data, and the experimental intensity curves were combined into a single curve covering $1.25 \leq s \leq 42$ Å^{-1} by adding the curves in the overlap region weighted by $\cos^2 [\pi(s - s_{min})/2(s_{max} - s_{min})]$ and $\sin^2 [\pi \cdot (s - s_{min})/2(s_{max} - s_{min})]$ for the smaller and larger angle data sets, respectively. s_{min} is the minimum s value of the larger angle data and s_{max} is the maximum s value of the smaller angle data. A radial distribution function was calculated from this curve and the background was refined until the distribution function showed no significant fluctuations in nonstructural regions. Values and standard deviations for structural parameters were obtained from a least-squares analysis of the intensity curve using a program written by Dr. Hans Seip.[13] The theoretical intensity was given by the form

$$sM_{th}(s) = \sum_i\sum_j Z_i Z_j A_{ij} \exp(-l_{ij}^2 s^2/2) \sin sr_{ij}/r_{ij}$$

$$A_{ij} = (1 - F_i/Z_i)(1 - F_j/Z_j)/(Z_C - F_C)^2$$

where l_{ij} is the root-mean-square amplitude of vibration between atoms i and j. Reported errors for interatomic distance are the geometric means of three times the standard deviations obtained from the least-squares analysis, using a diagonal weight matrix, and three times an estimated standard deviation of $0.001 r_{ij}$ for scale errors. Correlation among data points was ignored. The reported errors for interatomic angles and vibrational amplitudes are three times

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the least-squares standard deviations since these parameters are unaffected by scale errors.

Results and Discussion

The experimental molecular intensity curve is shown in Figure 2 with the difference between it and the calculated curve for the best model. The radial distribution function calculated from the experimental intensity multiplied by $\exp(-0.001s^2)$ is shown in Figure 3 with the difference between it and the radial distribution function calculated from the best model. In the least-squares analysis of the molecular intensity curve eight parameters were used to define the molecule's structure (see Figure 4): four carbon–carbon bond lengths, C_1–C_2, C_2–C_3, C_1–C_4, and C_1–C_5; an average carbon–hydrogen bond length; the dihedral angle between the plane of the cyclopropane ring and the mean plane of the cyclobutane ring; an average H–C–H angle; and the dihedral angle of the cyclobutane ring. The dihedral angle was found to be 4.0° with a standard deviation of 5.5°. Therefore, the analysis was completed assuming a seven-parameter model in which the cyclobutane ring was constrained to be planar. Vibrational amplitudes were grouped according to distance type. All bonded C–C vibrational amplitudes were assumed equal and composed one group, and the bonded C–H and nonbonded C···C amplitudes composed two other sets. No other amplitudes could be simultaneously refined with the geometrical parameters and they were held fixed at reasonable values. After the scale factor, the seven geometrical parameters, and the three vibrational amplitudes had satisfactorily refined, studies were made on four angles determining the C–H bond directions. Two of these angles determine the direction of the bridgehead C–H bonds, another measures the deflection of the cyclobutane methylene groups away from each other, and the fourth measures the extent of twist of the cyclopropane CH_2 angle bisector from the cyclopropane ring plane. Projections of the least-squares residual function along an axis for each of the four angles were obtained in the following manner. Values were chosen for each of the four angles and several least-squares refinements of the 11 basic parameters were calculated until a minimum was obtained for the residual function. One angle was set to a new value and another series of refinements was carried out. The residual function value was thus obtained for a range of values of the angle under consideration and a value of the angle selected from the minimum of the projection. It was then held fixed and the second angle was systematically varied. This iterative process was continued for each of the four angles and the whole process recycled until none of the angles showed any significant change. Each projection of the residual function was a smooth concave-upward curve. There was no indication of any false minimum or complicated structure in the residual function in the vicinity of the least-squares minimum. The residual function projections are fairly flat in the region of the minimum and the angles are not accurately determined. This is consistent with the fact that the contributions to the scattered intensity from distances involving the hydrogen atoms are not great. The results of the data analysis are summarized in Table I. The molecule's structure is shown in Figure 4.
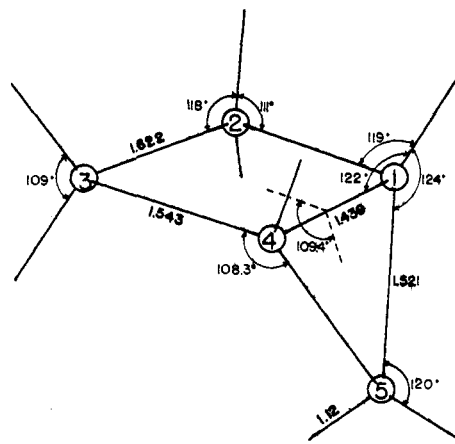

Figure 4. The structure of bicyclo[2.1.0]pentane.

The cyclobutane ring is planar within experimental error. Bicyclo[2.1.0]pentane is the first saturated compound to exhibit a planar conformation for the cyclobutane ring in the free molecule. Andersen[14] has deter-

Table I. Structural Parameters of Bicyclo[2.1.0]pentane

	$r_g(1)$,[a] Å	$r_g(0)$,[b] Å	l,[c] Å
C_1–C_2	1.541 (3)	1.543 ± 0.011	
C_1–C_5	1.519 (4)	1.521 ± 0.011	
C_1–C_4	1.437 (5)	1.439 ± 0.015	0.053 ± 0.008
C_2–C_3	1.620 (5)	1.622 ± 0.016	
C–H_{av}	1.111 (3)	1.121 ± 0.009	0.105 ± 0.008
C···C			0.068 ± 0.005
∠HCH_{av}, deg		108.8 ± 3.6[c]	
Dihedral angle, deg		109.4 ± 0.4[c]	

[a] The standard deviations listed in units of thousandths of an ångström in parentheses were obtained from the variance–covariance matrix derived using a diagonal weight matrix, i.e., data correlation was ignored, and are unrealistically small. [b] $r_g(0) = r_g(1) + l^2/r_g(1)$. The error limits were obtained from error $= [(3\sigma)^2 + (0.003r^2]^{1/2}$. [c] The error limits are 3σ.

mined that the cyclobutane rings in gaseous bicyclo[2.2.0]hexane are nonplanar, however. Wiberg and Barth[15] assumed a planar cyclobutane ring in endo-bicyclo[2.1.0]pentan-2-ol in a study of proton–proton coupling constants of it and related compounds and found that the coupling constants were consistent with a planar structure.

The average carbon–carbon bond length is 1.532 Å. The 1.543- and 1.521-Å C–C distances are typical of values found in cyclobutanes and cyclopropanes, respectively. The C_1–C_4 distance, 1.439 Å, is unusually short and the C_2–C_3 distance, 1.622 Å, is unusually long. Even though there is some uncertainty in the precise values of the C–C bond lengths due to their overlapping values, the results that C_2–C_3 is longer than a normal cyclobutane bond and especially that C_1–C_4 is unusually short are highly significant.

The very short zero-membered bridge, 1.44 Å, is the shortest C–C single bond yet observed in any saturated organic compound. Bak and Led[16] have developed a method for calculating bond lengths in three- and

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four-membered ring compounds based on atomic radii which are functions of the hybridization of the orbitals on the atom and which are projected onto the internuclear axis from the directions of the orbitals. The method requires information about the hybridization of the orbitals in the molecule, however, and there does not appear to be an unambiguous way of determining the hybridization of the orbitals in bicyclo[2.1.0]pentane on the basis of available data. Qualitatively, the very short distance is consistent with the bent bond method of Bak and Led. A shorter distance is predicted for bonds formed from orbitals with greater p character and the orbitals on the bridgehead carbon atoms forming bonds to other carbon atoms must have large p character because of the small bond angles. Also, the greater the angle between the internuclear axis and the orbitals composing the bond, the shorter the projection of the bond radius on the internuclear axis. If one considers bicyclo[2.1.0]pentane as cyclopropane with an ethylene bridge substituted for a pair of hydrogen atoms, then the orbitals in the zero-membered bridge bond are bent even farther from the internuclear axis than in cyclopropane. Support for the suggestion is found in a recent electron diffraction study of bicyclo[2.2.0]hexane.[14] In that compound the zero-membered bridge is the shortest C–C bond in the molecule. These arguments would predict an even shorter zero-membered bridge bond length in bicyclo[1.1.0]butane if the dihedral angle between the two rings were 109° and would predict a normal cyclopropane 1.515-Å[17] bond length for the bridge bond in bicyclo[3.1.0]hexane. The structure of the latter compound has not been studied, but the structure of bicyclo[1.1.0]butane has been determined.[18] The C–C bond lengths are 1.498 Å for the cyclopropyl side and 1.497 Å for the zero-membered bridge. The dihedral angle in bicyclo[1.1.0]butane is 122°, while in bicyclo[2.1.0]pentane it is 109°. An expansion of the dihedral angle causes the orbitals in the bridge bond to be directed more nearly along the internuclear axis, thereby lengthening the bond. Also, the angle strain seems to be more uniformly distributed throughout bicyclo[1.1.0]butane since the other C–C bond lengths are considerably shorter than in cyclopropane. In bicyclo[2.1.0]pentane, the bond lengths adjacent to the zero-membered bridge bond have normal values, suggesting that the strain is largely localized in the bridge bond.

The long C_2–C_3 bond length is consistent with findings in other four-membered ring compounds which have one short bond in the ring. The opposite distance is quite long in each case: 1.566 Å in cyclobutene,[19] 1.583 Å in cis-3,4-dichlorocyclobutene,[20] 1.584 Å in cis-3,4-dichlorobenzocyclobutene,[21] 1.60 Å in perfluorocyclobutene,[22] and 1.63 Å in hexamethyl(Dewar benzene).[23]

The dihedral angle in bicyclo[2.1.0]pentane is 109.4°. This is considerably smaller than the corresponding angle in norbornane, 125°.[24] A comparison of ^{13}C chemical shifts[25] in norbornane and bicyclo[2.1.0]pentane supports our result. The observed dihedral angle between the carbon ring and the plane containing cis C–H bonds in cyclopropane is 101.7°.[17]

The structural parameters are shown in Figure 4. The bridgehead C–H bond appears to make equal angles with all of the adjacent bonds. The angles are not precisely determined, however, and a study of the structure of 1,4-dimethylbicyclo[2.1.0]pentane was undertaken,[26] since the direction of the bridgehead C–C (methyl) is characterized more precisely by electron diffraction than is the direction of the corresponding C–H bond in bicyclo[2.1.0]pentane. The C–C (methyl) bond also forms equal angles with the other bonds about the bridgehead carbon. The cyclobutane methylene groups are bent away from each other toward the bridgehead carbons and the plane of the cyclopropane ring bisects the H–C_5–H angle.

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