in a 1 × 10 cm cylindrical quartz cell.[18] The rate constants at 1 and 740 mm are given in Table II. No large primary deuterium isotope effect is observed.

Table II. First-Order Gas-Phase Rate Constants for Bicyclopentene Isomerization

Substrate	$k \times 10^3$, sec^{-1} [a]	Pressure, mm[b]	No. of runs
H_6C_5	3.7 ± 1.2[c]	50–760	*d*
H_6C_5	2.8 ± 0.5	1	7
D_6C_5	1.2 ± 0.3	1	4
H_6C_5	2.8 ± 0.4	740	6
D_6C_5	2.5 ± 0.4	740	3

[a] At 80.0 ± 0.05°. [b] Bicyclic olefin diluted with propane. [c] Probable error. [d] Calculated from data in ref 2 and 3.

The labeling results and the small isotope effect on the rate constant for the isomerization rule out the orbital symmetry allowed retro-ene mechanism for the isomerization. They are consistent with the disrotatory, disallowed "biradical" process and with several other plausible formulations. A distinction among three of these is now being sought through the synthesis and rearrangement of bicyclopentene-*2,3-d*$_2$.

[18] The fair agreement between the present and earlier[2,3] kinetic results for unlabeled bicyclopentene, in spite of a threefold increase in the cell's surface-to-volume ratio, argues against a possible heterogeneous[2,3] process.

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The Microwave Spectrum, Structure, Molecular Dipole and Quadrupole Moments, and Magnetic Properties of Bicyclo[2.1.0]pent-2-ene

Sir:

We have assigned the microwave spectrum of homocyclobutadiene (**1**) and derived some structural information therefrom. We have also measured the electric dipole moment, the molecular *g* values, the magnetic susceptibility anisotropies, and the molecular quadrupole moments.

Bicyclo[2.1.0]pent-2-ene shown in Figure 1 was prepared by a modification of the known procedure[1] and was collected by preparative glpc in a carbon tetrachloride solution of *N*-phenylmaleimide. The sample was distilled directly from the solution at −80° into the microwave absorption cell[2,3] cooled also to Dry Ice temperature. The microwave spectrograph used has been described before[4] and 5-kHz Stark modulation was employed in the present investigation. The technique of searching for absorption lines was similar to that used earlier in our microwave study of cyclopropanone.[5] Bicyclo[2.1.0]pent-2-ene is stable in the waveguide at Dry Ice temperature although it was reported to have a short lifetime in solution at room temperature.[1] An initial assignment of the rotational spectrum of **1** was obtained on the strong $J = 1 \rightarrow 2$, *a* dipole-type transitions by their characteristic Stark effect. The observed and calculated transition frequencies are listed in Table I. A least-squares fit of all observed transition frequencies gives the rotational constants of $A = 10811.65 \pm 0.11$ MHz, $B = 6517.883 \pm 0.0025$ MHz, and $C = 5216.287 \pm 0.0024$ MHz. If we assume the four-membered ring in **1** to be planar as in cyclobutene,[6] the *a* and *c* principal inertial axes would lie in the plane of symmetry of **1**. The *a* axis is tilted about 22° from the plane of the four-membered ring. We were not able to observe the *c*-dipole transitions indicating that $\mu_c < \mu_a$.

Table I. Rotational Transitions in Bicyclo[2.1.0]pent-2-ene

Transition	Obsd ν,[a] MHz	(obsd − calcd[b])ν, MHz
0_{00}–1_{01}	11734.19	0.02
1_{11}–2_{12}	22166.75	0.01
1_{01}–2_{02}	23214.68	0.06
1_{10}–2_{11}	24769.92	−0.02
2_{12}–3_{13}	33104.42	−0.01
2_{02}–3_{03}	34245.47	−0.01
2_{21}–3_{22}	35202.53	0.02
2_{20}–3_{21}	36159.53	0.00
2_{11}–3_{12}	36977.55	−0.04
4_{14}–4_{13}	12799.54	0.01

[a] Estimated uncertainty: ±0.1 MHz. [b] Calculated from $A = 10811.65$, $B = 6517.883$, and $C = 5216.287$ MHz.

To deduce information on the molecular structure of **1**, initial structural parameters were taken from bicyclo[1.1.0]butane[7] and cyclopentadiene[8] (see also the structures of cyclopentene[9] and cyclobutene[6]). The three-membered ring C–C bond lengths and the dihedral angle between the two ring planes, α, were varied to fit the experimental moments of inertia, giving $R(C_1\text{–}C_4)_{\text{bridge}} = 1.56$ Å, $R(C_1\text{–}C_5) = 1.53$ Å, and $\alpha = 114°$. The calculated moments of inertia in amu-Å^2 are $I_a = 46.70$, $I_b = 77.45$, and $I_c = 96.68$ and can be compared with the experimental values of $I_a = 46.7583$, $I_b = 77.5618$, and $I_c = 96.9153$, also in amu-Å^2 (conversion unit used: 505375 MHz amu-Å^2). The best fit structure is shown in Figure 1.

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[1] J. I. Brauman, L. E. Ellis, and E. E. van Tamelen, *J. Amer. Chem. Soc.*, 88, 846 (1966); A. H. Andrist, J. E. Baldwin, and R. K. Pinschmidt, Jr., submitted for publication. For this study **1** was prepared by photolysis of cyclopentadiene in 1,4-dioxane followed by preparative glpc on a 5 m × 6 mm 21% β,β'-oxydipropionitrile on an aluminum Chromosorb P column at 25°.

[2] *N*-Phenylmaleimide effectively stabilizes solutions of **1** by removing cyclopentadiene; *cf.* J. E. Baldwin and R. K. Pinschmidt, Jr., *J. Amer. Chem. Soc.*, **92**, 5247 (1970).

[3] The vapor pressure of **1** at −80° is 45 μ. Reversion of **1** to cyclopentadiene proceeds at a significantly enhanced rate in the brass waveguide above −80° when compared with the rate of isomerization in a quartz vessel.

[4] W. H. Flygare, *J. Chem. Phys.*, **41**, 206 (1964); M. L. Unland, V. M. Weiss, and W. H. Flygare, *ibid.*, **42**, 2138 (1965).

[5] J. M. Pochan, J. E. Baldwin, and W. H. Flygare, *J. Amer. Chem. Soc.*, **90**, 1072 (1968); **91**, 1896 (1969).

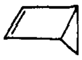
[6] H. Kim and W. D. Gwinn, *J. Chem. Phys.*, **42**, 3728 (1965); B. Bak, J. J. Led, L. Nygaard, J. Rastrup-Andersen, and G. O. Sorensen, *J. Mol. Struct.*, **3**, 369 (1969).

[7] M. D. Harmony and K. W. Cox, *J. Amer. Chem. Soc.*, **88**, 5049 (1966); K. W. Cox, M. D. Harmony, G. Nelson, and K. B. Wiberg, *J. Chem. Phys.*, **50**, 1976 (1969).

[8] L. H. Scharpen and V. W. Laurie, *ibid.*, **43**, 2765 (1965).

[9] S. S. Butcher and C. C. Costain, *J. Mol. Spectr.*, **15**, 40 (1965).

The electric dipole moment was measured by standard observations[10] of the Stark effect on the $1_{11} \rightarrow 2_{12}$ ($M = 0$), $1_{01} \rightarrow 2_{02}$ ($M = 1$), and $1_{01} \rightarrow 2_{02}$ ($M = 0$) transitions. The $J = 1 \rightarrow 2$, $M = 0$ transition of OCS[11] was used to calibrate the electric field strength in the absorption cell. The resultant moments were $\mu_a = 0.398 \pm 0.01$ D and $\mu_c = 0.025 \pm 0.002$ D. Thus, the total dipole is aligned very close to the a principal inertial axis with a value of $\mu = 0.398 \pm 0.01$ D. It is interesting to note the variation in the magnitude of the electric dipole moments in comparable molecules as shown below.

	0.398 ± 0.01 D	(this work)
	0.675 ± 0.01 D	(ref 7)
	0.190 ± 0.01 D	(ref 9)
	0.132 ± 0.01 D	(ref 6)
	0.419 ± 0.01 D	(ref 8)

In addition to the above molecular parameters, the molecular rotational Zeeman effect was also measured[12] which gives directly the molecular g values and magnetic susceptibility anisotropies.[13] Combining these parameters with the rotational constants (A, B, and C) gives the molecular quadrupole moments.[13] These values are listed below in Table II with the corresponding values for cyclobutene.[14]

Table II. Molecular g Values, Magnetic Susceptibility Anisotropies,[a] and Molecular Quadrupole Moments[b]

	Bicyclo[2.1.0]pent-2-ene	Cyclobutene[c]
g_{aa}	−0.0046 ± 0.0019	−0.0516 ± 0.0007
g_{bb}	−0.0342 ± 0.0011	−0.0663 ± 0.0006
g_{cc}	−0.0218 ± 0.0012	−0.0219 ± 0.0006
$2\chi_{aa} - \chi_{bb} - \chi_{cc}$	−14.9 ± 1.1	−0.9 ± 0.5
$-\chi_{aa} + 2\chi_{bb} - \chi_{cc}$	+7.8 ± 1.5	+5.0 ± 0.7
Q_{aa}	−1.9 ± 1.5	−0.3 ± 0.6
Q_{bb}	+2.7 ± 1.7	+1.6 ± 0.7
Q_{cc}	−0.8 ± 2.4	−1.3 ± 1.0

[a] In units of 10^{-6} erg/G^2 mol. [b] In units of 10^{-26} esu-cm^2. [c] The a axis in cyclobutene bisects the carbon–carbon double bond with a and b axes in the molecular plane.

The results of Table II indicate that **1** and cyclobutene possess similar magnetic properties and similar electric charge distributions. Values of $\chi_{cc} - {}^1/_2(\chi_{aa} + \chi_{bb})$ are also similar: +3.6 ± 1.4 for **1** and −2.0 ± 0.6 for cyclobutene. These anisotropies ($\chi_{cc} - {}^1/_2(\chi_{aa} + \chi_{bb})$) contrast sharply with the corresponding value of −34.3 in cyclopentadiene.[14,15] This large value of $\chi_{cc} - {}^1/_2(\chi_{aa} + \chi_{bb})$ in cyclopentadiene apparently indicates a ring current in this conjugated system.[16,17]

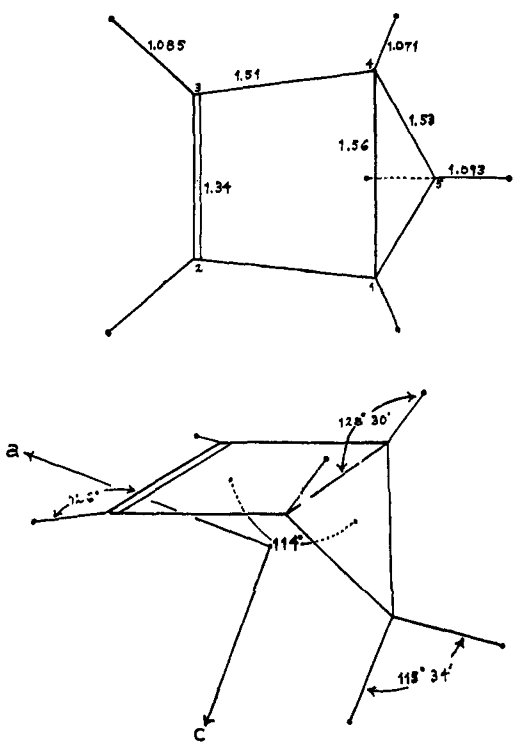


Figure 1. The molecular structure of bicyclo[2.1.0]pent-2-ene.

The small values of $\chi_{cc} - {}^1/_2(\chi_{aa} + \chi_{bb})$ in **1** and cyclobutene indicate small electron delocalization in these molecules relative to the apparent large electron delocalization in cyclopentadiene.[18,19]

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(10) S. Golden and E. B. Wilson, Jr., *J. Chem. Phys.*, **16**, 669 (1948).

(11) J. S. Muenter, *ibid.*, 48, 4544 (1968).

(12) For a description of the apparatus see: W. H. Flygare, W. Hüttner, R. L. Shoemaker, a nd P. D. Foster, *ibid.*, **50**, 1417 (1969).

(13) W. Hüttner and W. H. Flygare, *ibid.*, **47**, 4137 (1967), and W. Hüttner, M. K. Lo, and W. H . Flygare, *ibid.*, **48**, 1206 (1968).

(14) R. C. Benson and W. H. Flygare, *ibid.*, in press.

(15) See ref 14; the numbers are cited in ref 16.

(16) J. H. S. Wang and W. H. Flygare, *J. Chem. Phys.*, **52**, 5636 (1970).

(17) J. M. Pochan and W. H. Flygare, *J. Amer. Chem. Soc.*, **91**, 5928 (1969).

(18) D. H. Sutter and W. H. Flygare, *ibid.*, **91**, 4063 (1969).

(19) D. H. Sutter and W. H. Flygare, *ibid.*, **91**, 6895 (1969).

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Intermediates in the Titanocene-Promoted Fixation-Reduction of Molecular Nitrogen

Sir:

Lower valent titanium species play an important role in the fixation of molecular nitrogen (N_2) under mild conditions, and have moved to center stage because of the chemical mutability of their nitrogen ligands and the mechanistic accessibility of these systems. Expressly basing experiments on the concept of titanium(II)[1] as the N_2-fixing type, this laboratory first reported: (1) the titanocene–naphthalide (Np) and

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(1) E. E. van Tamelen and M. A. Schwartz, *J. Amer. Chem. Soc.*, **87**, 3277 (1965).