nitrile oxide with 2-bromoethylamine (freshly liberated from its hydrobromide at low temperatures) yielded the bromo amidoxime (IIb), which, when treated with concentrated aqueous sodium hydroxide, furnished a compound identical in all respects with IIIa.

In trying to establish whether the formation of IIIa from Ia proceeded in a single step or through two discrete steps, we were able to isolate the intermediate chloro amidoxime (IIa) as its hydrochloride and cyclize it to IIIa with base. Hence, this reaction cannot be termed a rearrangement in the formal sense of the term.

Since the 1-aroylaziridine oximes Ib–e can also be converted, in a similar fashion, into compounds IIIb–e, this sequence of reactions constitutes a new method for the synthesis of 1,2,4-oxadiazine derivatives.

It is pertinent to mention here that the 1-aroylaziridine oximes (Ia–e) do not undergo any type of isomerization in the presence of the nucleophilic iodide ion.[1]

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Microwave Spectrum, Dipole Moment, and Structure of Bicyclo[1.1.0]butane

Sir:

Since bicyclo[1.1.0]butane was first synthesized in 1963,[1,2] many of the physical and chemical properties of this interesting bicyclic species have been elucidated. Wiberg[3] has given a good review of much of this work. It is particularly interesting that the molecule has the largest strain energy per carbon atom of any known molecule.[3] In this regard, it is of interest to know, also, the geometrical structure and electronic distribution of bicyclobutane. Haller and Srinivasan[4] obtained some structural information from the analysis of partially resolved infrared vibration–rotation bands, but the method cannot be expected to give results of high accuracy. In order to obtain accurate values of the structural parameters, we have begun an investigation of the microwave (rotational) spectrum of bicyclobutane. In this article we wish to report microwave spectroscopic measurements of the dipole moment and some preliminary structural calculations based on the normal isotopic species, $^{12}C_4H_6$.

The sample used in this study was prepared by the method of Wiberg and Lampman.[5] An infrared spectrum of the gas agreed well with that reported by Haller and Srinivasan.[4] The microwave spectrum of the normal isotopic species has been studied, the most startling feature of this spectrum being the relatively high intensity of the observed absorption lines. Table I lists some of the observed rotational transitions and the rotational constants which were obtained by the usual rigid rotor analysis.[6] The goodness of the fit may be seen in Table I by comparing the observed frequencies with those calculated from the derived rotational constants. All the observed lines were *c* type; that is, their intensities are proportional to the square of the component of the molecular dipole moment along the inertial *c* axis. No *a*- or *b*-type transitions were observed, which is in accord with the C_{2v} symmetry of the molecule.[4] It should be mentioned that the rotational constants reported by Haller and Srinivasan[4] are in remarkably good agreement with those given in Table I considering the difficulties encountered in analyzing partially resolved vibration–rotation bands.

Table I. Rotational Transitions and Rotational Constants of Bicyclobutane

Transition	Observed[a]	Calculated
$0_{00} \rightarrow 1_{10}$	26,625.55	26,625.50
$1_{10} \rightarrow 2_{02}$	26,420.63	26,420.72
$2_{11} \rightarrow 2_{21}$	23,995.38	23,995.40
$3_{12} \rightarrow 3_{22}$	22,664.28	22,664.27
$4_{13} \rightarrow 4_{23}$	20,927.71	20,927.74
$2_{12} \rightarrow 2_{20}$	26,830.19	26,830.27
	A 17,311.98 Mc/sec	
	B 9,313.51 Mc/sec	
	C 8,393.52 Mc/sec	

[a] Observed and calculated frequencies have units of Mc/sec. Estimated uncertainty of observed frequencies is less than ±0.1 Mc/sec.

The dipole moment of the molecule has been determined by studying the shifts, $\Delta\nu$, of the $0_{00} \rightarrow 1_{10}$ and $2_{11} \rightarrow 2_{21}$ ($M = 2$) transitions as a function of electric field, E (the quadratic Stark effect). The experimental values of $\Delta\nu/E^2$, 2.198×10^{-6} and 1.140×10^{-6} Mc/sec (v/cm)^2, respectively, give, by use of the theory of Golden and Wilson,[7] the value 0.675 ± 0.01 D. for the dipole moment of the molecule (along the C_2 axis). This value agrees well with that obtained by similar, but less accurate, measurements on the $1_{10} \rightarrow 2_{02}$ transition.

It is difficult to account in a simple way for such a large dipole moment in this saturated hydrocarbon. Since it is unlikely that the entire dipole moment can be produced by the heteropolar C–H bond dipoles (cancellations of methylene and bridgehead C–H dipoles should be effective), electronic charge must be distributed unequally in or near the homopolar C–C bonds. Relatively small differences in hybridization of the bridgehead and ring C–C bonds may produce an appreciable skeletal dipole moment by means of the atomic dipole and overlap moments discussed by Coulson and Rogers.[8]

The rotational constants obtained in this study are not sufficient for a complete structural analysis. If, however, all parameters needed to locate the hydrogen nuclei relative to the carbon skeleton are assumed,

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(1) D. M. Lemal, F. Menger, and G. W. Clark, *J. Am. Chem. Soc.*, **85**, 2529 (1963).

(2) R. Srinivasan, *ibid.*, **85**, 4045 (1963).

(3) K. B. Wiberg, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **26**, 143 (1965).

(4) I. Haller and R. Srinivasan, *J. Chem. Phys.*, **41**, 2745 (1964).

(5) K. B. Wiberg and G. M. Lampman, *Tetrahedron Letters*, 2173 (1963).

(6) C. H. Townes and A. L. Schawlow, "Microwave Spectroscopy," McGraw-Hill Book Co., Inc., New York, N. Y., 1955.

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

(8) C. A. Coulson and M. T. Rogers, *ibid.*, **35**, 593 (1961).

then the bridgehead and ring C–C distances, and the dihedral angle, α, between the ring planes, may be chosen to reproduce the experimentally observed rotational constants. For this purpose we have chosen all $R(\text{CH}) = 1.08$ A, and $\angle\text{HCH} = 116°$, with the HCH angles bisected by the ring planes. The bridgehead CCH angles are much more uncertain but were chosen such that each bridgehead C–H bond was oriented at identical angles to all three adjacent C–C bonds.[9] With these assumptions, the best fit gives $\angle\text{CCH}$ (bridgehead) = 130°, $R(\text{CC})_{\text{bridge}} = 1.49$ A, $R(\text{CC})_{\text{ring}} = 1.51$ A, and $\alpha = 121°$. If $\angle\text{CCH}$ (bridgehead) is opened up to 145° (Haller and Srinivasan[4] suggested 160°), the major change is to force $R(\text{CC})_{\text{bridge}}$ to become even smaller, about 1.44 Å. It seems likely that $R(\text{CC})_{\text{bridge}}$ is indeed smaller than $R(\text{CC})_{\text{ring}}$, indicating that the bridgehead bond is somewhat stronger and has a somewhat higher electron density. This would be in agreement with some chemical reactivity results discussed by Wiberg[3] and would also be an important factor in contributing to the large dipole moment. We are currently studying other isotopic species of bicyclobutane in order to resolve the structural problem completely.

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[9] The assumption is arbitrary but might have physical reality if nonbonded interactions of the bridgehead hydrogens with the nearest neighbor carbon atoms were important.

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Energy Transfer in Ion-Impact Mass Spectra. Application to Structural Mass Spectrometry[1]

Sir:

We have investigated the problem of energy transfer in ion-impact mass spectra to determine its potential as a technique for structural studies on complex molecules. Electron-impact ionization techniques have been used extensively to provide information on molecular structures.[2-4] Electron impact produces excited ionized species which decompose unimolecularly to yield mass spectra, but many isomeric and closely related molecules are virtually indistinguishable because the excitation deposited in electron-impact ionization is frequently sufficient to obscure subtle differences in molecular structure. Ion impact, on the other hand, provides a means of depositing energy by an over-all mechanism which is significantly different from that operative in electron impact and which permits a more precise control of the magnitude of the excitation in the target molecule. The bulk of the energy deposited in ion-impact processes, if relatively low velocity ions are used as projectiles, comes from the recombination energy of the projectile ion.[5] Additional energy can be deposited locally at the point of impact between the colliding molecules by conversion of projectile ion translational energy into target molecule internal energy.[6] If it is desired to demonstrate differences in decomposition patterns between isomeric molecules, the ideal projectile must have a recombination energy very close to the ionization potential of target isomers, and the additional energy to produce the ion fragments should then come from translational energy of the projectile. The success of such an approach depends on the validity of the assumption that kinetic energy deposited locally in a molecule ion sets up a forced vibration which favors dissociation prior to redistribution of this excess energy among other internal degrees of freedom in the target molecule ion. If a statistical distribution of energy takes place prior to decomposition then mass spectra similar to those obtained by electron impact would be expected.

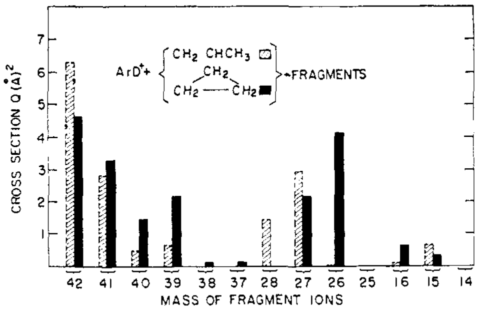

Figure 1. Ion-impact mass spectrum produced in collisions of 10-ev ArD$^+$ ions with propylene and cyclopropane. Reaction cross sections, in units of square angstroms, are plotted for the different fragment ions.

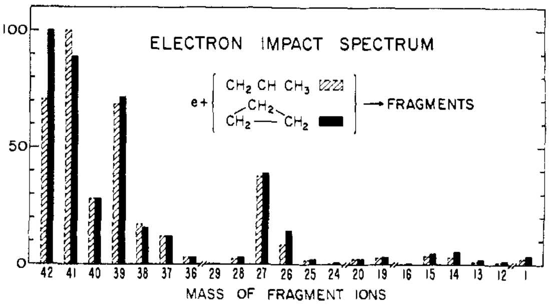

Figure 2. Electron-impact spectrum of propylene and cyclopropane.

We have determined ion-impact mass spectra of isomeric butenes, propylene, and cyclopropane using low-velocity ArD$^+$, COD$^+$, and Ar$^+$ ions as projectiles. These data[7] will be discussed in more detail in a subsequent publication. Results obtained with 10-ev ArD$^+$ ions on propylene and cyclopropane are presented in Figure 1. Electron-impact mass spectra

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[1] Research performed under the auspices of the U. S. Atomic Energy Commission.

[2] F. A. Long and L. Friedman, *J. Am. Chem. Soc.*, **75**, 2837 (1953).

[3] K. Biemann, "Mass Spectrometry: Organic Chemical Applications," McGraw-Hill Book Co., Inc., New York, N. Y., 1963.

[4] F. W. McLafferty in "Determination of Organic Structures by Physical Methods," F. C. Nachod and W. D. Phillips, Ed., Academic Press Inc., New York, N. Y., 1962.

[5] E. Lindholm, I. Szabo, and P. Wilmenius, *Arkiv Fysik*, **25**, 417 (1963).

[6] C. F. Giese and W. B. Maier, II, *J. Chem. Phys.*, **39**, 197 (1963).

[7] The ion beams used in these studies were generated and mass analyzed with a 60-in. radius, 90° sector electromagnetic isotope separator, retarded and injected into an ion source attached to a 6-in., 60° Nier-type mass spectrometer.