would be achieved within the interior of helices if the hydrogen bonds were displaced to the side of the C=O group. Distortions of this kind have been observed in certain regions of lysozyme[14] and in myoglobin[15] and have also been predicted theoretically.[14]

In summary the ORD and CD spectra of ribonuclease indicate that its helical contributions are at lower wavelengths than those in polypeptide models and in many proteins. Most of the literature on optical rotation has emphasized the role of conformation on the magnitude and sign of Cotton effects. We are here dealing as well with the effect of conformation and solvation on the energy of the transition which produces the Cotton effect. Hydrogen bonds involving the n orbitals produce such changes, and it is suggested that the n,π^* Cotton effects of helices which are very short or badly distorted will be displaced toward lower wavelengths as in ribonuclease.[15a]

Acknowledgment. We are grateful to J. T. Yang for permitting us to use his instrument for the measurement of circular dichroism.

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(15a) NOTE ADDED IN PROOF. Since this paper was submitted, we have learned of the complementary work of B. Jirgensons (*J. Am. Chem. Soc.*, **89**, 5979 (1967)). Noting that the position of the trough is not that of an α helix, he has used the peak in the ORD spectrum at 199 mμ to estimate helix content.

(16) Public Health Service Predoctoral Fellow.

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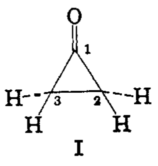
Received July 5, 1967

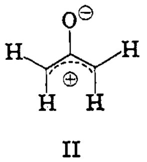
Microwave Spectrum, Structure, and Dipole Moment in Cyclopropanone

Sir:

Various substituted cyclopropanones react with dienes such as furan to give cycloadducts;[1-6] the adducts are formally ascribable to either a 4 + 2 cycloaddition of diene across the C_2–C_3 single bond of the cyclopropanone (I) or a 4 + 3 addition of diene and an acyclic dipolar reactive intermediate (II). Both reaction modes would be, according to orbital symmetry conditions, thermally allowed for *cis* cycloadditions.[7]



I



II

Extended Hückel calculations[8] have suggested that the ring-closed form I may be unstable relative to the oxyallyl acyclic dipolar structure II. In fact, the approximate calculations give no stability for cyclopropanone with respect to conversion to oxyallyl.[8]

We now report clear-cut spectroscopic evidence for ring-closed cyclopropanone (I). Microwave transitions for the compound thought to be cyclopropanone, prepared from ketene and diazomethane[9] in fluorotrichloromethane, were observed in several microwave absorption cells. The microwave spectrograph has been described before.[10,11] Considerable difficulty was experienced in maintaining the quality of the spectra above Dry Ice temperatures. Known rotational transitions for acetone,[12] ketene,[13] and fluorotrichloromethane[14] were observed. No transitions were observed for cyclobutanone,[15] acrolein,[16] or diazomethane.[17] Rotational transitions of the new molecule were identified by the Stark effect. Only transitions excited by the dipole moment along the axis of least moment of inertia (*a*, principal inertial axis) were observed. The assigned *a*-type transitions, rotational constants, and calculated transitions are listed in Table I. The μ_b- and μ_c-type rotational transitions were also predicted, and a careful search was made to find these lines. No μ_b or μ_c transitions were observed, which indicates the molecule has C_{2v} symmetry. The Stark effect was observed with high precision as a function of electric field for the $1_{10} \rightarrow 2_{11}$ and $0_{00} \rightarrow 1_{01}$ transitions. The above Stark effect gives an electric dipole moment in this molecule of $\mu_a = 2.67 \pm 0.10$ D which is intermediate between the

Table I. Observed and Calculated Rotational Transitions in Cyclopropanone[a]

Transition	Frequencies Obsd	 Calcd
0(0,0)-1(0,1)	13,338.6	13,338.4
1(1,1)-2(1,2)	25,082.1	25,082.1
1(1,0)-2(1,1)	28,271.6	28,271.4
1(0,1)-2(0,2)	26,535.8	26,535.7
2(0,2)-3(0,3)	39,458.0	39,458.1
2(2,1)-3(2,2)	40,014.8	40,015.1
2(1,2)-3(1,3)	37,538.7	37,538.6
3(1,3)-3(1.2)	9,560.4	9,560.0
6(2,5)-6(2,4)	8,623.6	8,623.0
6(1,6)-6(1,5)	32,847.6	32,847.6
7(2,6)-7(2,5)	14,329.8	14,329.5
9(2,8)-9(2,7)	30,697.0	30,697.5

[a] The calculated transitions are for A = 20,153.8 ± 1.0 MHz, B = 7466.50 ± 0.05 MHz, and C = 5871.87 ± 0.05 MHz which were obtained by a least-squares fit of the observed frequencies. Experimental errors are estimated to be 0.1 MHz.

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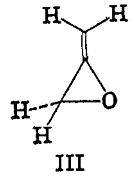
values of 2.93 and 2.34 in acetone[12] and formaldehyde,[18] respectively.

The moments of inertia are easily determined from the rotational constants in Table I, giving $I_a = 25.1$ amu Å^2, $I_b = 67.70$ amu Å^2, and $I_c = 86.10$ amu Å^2. These moments indicate that most of the mass is contained in a plane. The combination of moments, $(I_a + I_b - I_c)$, leads to the value of $2\Sigma_i m_i c_i^2 = 6.70$ where m_i is the mass of the ith nucleus and c_i is the distance of the ith particle along the c axis (axis of largest moment of inertia). The values of $(I_a + I_b - I_c)$ are listed in Table II for several molecules with known out-of-plane protons. There seems to be no doubt that the present molecule has four out-of-plane protons. Note the similarity in Table II for the values of $(I_a + I_b - I_c)$ in ethylene oxide and the present molecule. If we assume $\Sigma_i m_i c_i^2$ is caused by four hydrogen atoms we get $c_H = 0.91$ Å. If we further assume that the molecule has two identical HCH structural subunits as in ethylene oxide with a H–C distance of 1.085 Å, we obtain a HCH angle of 115 ± 3°, which is again close to the result in ethylene oxide or the cyclopropanes. Thus, this simple analysis points strongly toward a simple ring-closed structure of cyclopropanone with three carbon atoms and one oxygen atom in a plane and four protons out of the plane (I). Another possible structure, allene oxide (III), is ruled out: only two protons are out of the plane, and two dipole components would have been observed as in methylcyclopropene.[19]

Table II. $(I_a + I_b - I_c)$ for Several Molecules[a]

Molecule	$(I_a + I_b - I_c)$	No. of out-of-plane protons	Ref
trans-Acrolein	0.0212	0	16
1,2,5-Oxadiazole	0.0707	0	*b*
Furan	−0.0481	0	*c*
Cyclopropene	3.31	2	*d*
Cyclopentadiene	3.11	2	*e*
Ethylene oxide	6.83	4	*f*
β-Propiolactone	6.50	4	*g*
Cyclopropanone	6.70	4	*h*

[a] In atomic mass units ångströms squared. [b] E. Sagebarth and A. P. Cox, *J. Chem. Phys.*, **43**, 166 (1965). [c] M. H. Sirvetz, *ibid.*, **19**, 1609 (1951). [d] P. H. Kasai, R. J. Myers, D. F. Eggers, Jr., and K. B. Wiberg, *ibid.*, **30**, 512 (1959). [e] V. W. Laurie, *ibid.*, **24**, 635 (1956). [f] G. L. Cunningham, Jr., A. W. Boyd, R. J. Myers, and W. D. Gwinn, *ibid.*, **19**, 676 (1951). [g] N. Kwak, J. H. Goldstein, and J. W. Simmons, *ibid.*, **25**, 1203 (1956). [h] This work.



III

Further manipulation with the moments of inertia shows that the C_2–C_3 distance is larger than the C_1–C_2 and C_1–C_3 distances.[20] A structure which fits the observed moments is listed in Table III. Further work on this molecule, including a complete isotopic structure analysis, is in progress.

Table III. Structural Parameters for Cyclopropanone[a]

Bond	Length, Å	Angle
C_1–O	1.18	$C_3C_1C_2$, 64°
C_1–$C_{2,3}$	1.49	HCH, 117° 35′
C_2–C_3	1.58	
$C_{2,3}$–H_{1-4}	1.085	

[a] The HCH plane bisects the CCC angle. The molecule has C_{2v} symmetry. Calculated moments of inertia (amu Å^2): $I_a = 25.060$, $I_b = 68.040$, $I_c = 86.155$. Experimental moments of inertia (amu Å^2): $I_a = 25.1$, $I_b = 67.70$, $I_c = 86.10$.

There appears to be little doubt that cyclopropanone (I) has been isolated and identified. There is also no doubt that the molecule identified herein is in a singlet ground state. The observed spectrum shows no magnetic hyperfine structure as is characteristic of radicals. In addition, we have observed the $2_{21} \rightarrow 3_{22}$ transitions (Table I) in a high magnetic field (11,000 gauss).[21] The zero-field line was 300 kHz at half-height. No additional splitting or broadening was observed at the high magnetic field.

Acknowledgment. The support of the National Science Foundation is gratefully acknowledged.

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(22) (a) Standard Oil of California Fellow; (b) Alfred P. Sloan Fellow.

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Received December 11, 1967

Mass Spectral Fragmentation of Aniline-1-^{13}C[1]

Sir:

The major electron impact fragmentation pathway of aniline is that shown in eq 1,[2] as demonstrated by studies with aniline-^{15}N.[3] In view of the well-documented rearrangement of toluene in its mass spectral fragmentation (eq 2), most readily explained by a tropylium ion intermediate (I),[1,4,5] we have examined the possible intermediacy of an analogous azepinium ion (IIa) in the fragmentation of aniline[6] by studying

$$\underset{m/e\ 93}{C_6H_7N\cdot^+} \xrightarrow[m^*]{-HCN} \underset{m/e\ 66}{C_5H_6\cdot^+} \tag{1}$$

$$\underset{m/e\ 92}{C_7H_8\cdot^+} \xrightarrow{-H\cdot} \underset{m/e\ 91}{C_7H_7^+} \xrightarrow{-C_2H_2} \underset{m/e\ 65}{C_5H_5^+} \tag{2}$$

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(1) Presented in part at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 11–15, 1967, Paper No. S-85.

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(6) Rylander, *et al.*, found "a proposal of ring expansion less attractive in aniline than in toluene."[3] However, thiepinium, oxepinium, and azatropylium ions have been postulated as intermediates in the mass spectral fragmentation of thiophenol,[7] *meta*- and *para*-substituted phenetoles,[8] picolines,[9] and methylquinolines and -isoquinolines.[10]