The Microwave Spectrum, Structure and Bonding, and Barrier to Internal Rotation in 1-Methylcyclopropene

Sir:

1-Methylcyclopropene was synthesized by the method given by Fisher and Applequist,[1] and purification was achieved by several bulb-to-bulb vacuum distillations. Comparison with known infrared and nuclear magnetic resonance spectra[2] showed only trace impurities, and the microwave spectrum was recorded[3] and assigned without further purification. Several of the rotational transitions were split into doublets due to the hindered internal rotation of the methyl group. The observed transitions and splittings are given in Table I. The rigid rotor fit of the A torsional-state transitions leads to rotational constants (Mc/sec) of $A = 20{,}556.19 \pm 0.12$, $B = 6356.98 \pm 0.02$, and $C = 5176.42 \pm 0.02$.

Table I. Observed and Calculated Microwave Transitions and A–E Splittings in 1-Methylcyclopropene[a]

Transition	ν_{Aobsd}	ν_{Acalcd}	$(\nu_A - \nu_E)_{\text{obsd}}$	$(\nu_A - \nu_E)_{\text{calcd}}$
0(0,0) → 1(0,1)	11533.515	11533.402	$<\|0.020\|$	+0.010
0(0,0) → 1(1,1)	25732.61	25732.612	+10.87	+10.857
1(0,1) → 2(0,2)	22996.370	22996.211	$<\|0.080\|$	+0.072
1(1,1) → 2(1,2)	21886.307	21886.244	−0.919	−0.813
1(1,0) → 2(1,1)	24247.539	24247.365	+0.935	+0.850
2(1,2) → 3(1,3)	32786.000	32786.492	−0.230	−0.082
2(0,2) → 3(0,3)	34319.787	34319.497	+0.161	+0.225
2(2,1) → 3(2,2)	34599.990	34600.207	−33.69	−33.121
2(2,0) → 3(2,1)	34880.955	34880.918	+33.57	+32.966
2(1,1) → 3(1,2)	36325.494	36325.529	+0.342	+0.192

[a] The calculated ν_A transitions (in Mc/sec) are from $A = 20{,}556.19$, $B = 6356.98$, and $C = 5176.42$. The calculated splittings are from $V_3 = 1390$ cal/mole. All frequencies are in Mc/sec.

The extraction of a threefold barrier hindering the internal rotation of the methyl group is straightforward[4,5] and gives a barrier of $V_3 = 1390 \pm 50$ cal/mole. The observed and calculated A–E splittings are also shown in Table I.

In order to determine the C_2–C_4 distance and $C_1C_2C_4$ angle (see Figure 1) we have used the skeletal cyclopropene structure as determined by Kasai, Meyers, Eggers, and Wiberg.[6] The effect on the ring structure of substituting the methyl group in place of a hydrogen atom should be negligible. It has been shown, for instance that the C=C bond distances in ethylene[7] and propylene[8] are equal within the experimental errors of three to four parts per thousand. The results of the calculation are shown in Table II. The methyl group was assumed to be eclipsed to the C=C link.[8]

Calculated rotational constants (Mc/sec) from this structure are $A = 20{,}556.3$, $B = 6355.4$, $C = 5176.9$, which agree well with the experimental results. The rotational constants could also be matched by assuming a staggered methyl configuration, but the calculated structural parameters remain essentially unchanged (C_2–C_4 = 1.479 A, $<C_1C_2C_4 = 153°\ 12'$, $\theta = 33°$).

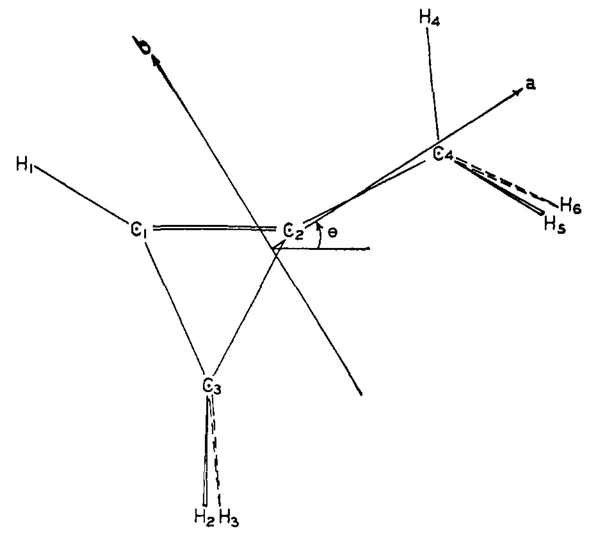

Figure 1.

Table II. Structural Parameters for 1-Methylcyclopropene[a]

Bond	Length, A	Angle	Size	θ
	Assumed Structural Parameters			
C_1–H_1	1.070	$H_1C_1C_2$	150°	
C_1–C_3	1.515	$H_2C_3H_3$	114° 42′	
C_1–C_2	1.300	$C_1C_3C_2$	50° 48′	
C_3–$C_{2,3}$	1.087	$C_2C_4H_4$	111°	
C_4–H_4	1.085			
C_4–$H_{5,6}$	1.098	$H_4C_4H_{5.6}$	109°	
	Calculated Structural Parameters			
C_2–C_4	1.476	$C_1C_2C_4$	152° 48′	33° 8′

[a] See Figure 1 for numbering of atoms.

The C_2–C_4 bond distance of 1.476 A reported here is shorter than the C–C bond distance of 1.501 A in propylene[8] and is closer to the corresponding C–C bond distance of 1.459 A in methylacetylene.[9]

The bonding in cyclopropane and cyclopropene has been discussed by Bernett[10] where he shows the equivalence between the Walsh[11] (W) and Coulson and Moffitt[12] (CM) bonding schemes for these molecules. However, the equivalence of the two models is only valid by assuming that the atomic orbitals do not overlap with their neighbors and that there are an equal number of electrons in each combining hybrid orbital in the W scheme. Employing these two assumptions, a linear transformation on the W orbitals then yields the CM hybrid orbitals. If there are not equal ionic parameters in the two in-ring W orbitals, a linear combination will not yield the CM orbitals. We will use the W orbital description in our following discussion. Under the conditions stated above these orbitals are equivalent to the CM description.[13]

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(1) F. Fisher and D. E. Applequist, *J. Org. Chem.*, 30, 2089 (1965).

(2) F. Fisher, Ph.D. Thesis, University of Illinois, 1965.

(3) See W. H. Flygare, *J. Chem. Phys.*, 41, 206 (1964), for a description of the microwave spectrograph.

(4) D. R. Herschbach, *ibid.*, 31, 91 (1959).

(5) R. G. Lett, Ph.D. Thesis, University of Illinois, 1966; R. G. Lett and W. H. Flygare, *J. Chem. Phys.*, in press.

(6) P. H. Kasai, R. J. Meyers, D. F. Eggers, Jr., and K. B. Wiberg, *ibid.*, 30, 512 (1959).

(7) L. S. Bartell and R. A. Bonham, *ibid.*, 31, 400 (1959).

(8) R. L. Lide, Jr., and D. Christensen, *ibid.*, 35, 1375 (1961).

(9) C. C. Costain, *ibid.*, 29, 864 (1958).

(10) W. H. Bernett, *J. Chem. Educ.*, 44, 17 (1967).

(11) A. D. Walsh, *Trans. Faraday Soc.*, 45, 179 (1949).

(12) C. A. Coulson and W. E. Moffitt, *J. Chem. Phys.*, 15, 151 (1947); *Phil. Mag.*, 40, 1 (1949).

The structural data on 1-methylcyclopropene indicates an sp-type hybrid at C$_2$. The C$_2$–C$_4$ bond distance (longer than methylacetylene[8] and shorter than propylene[6]) can be explained by allowing more p character in the C$_2$–C$_4$ bond with a corresponding lengthening over pure sp and more s character in the orbital directed into the ring. The HCH angle at C$_3$ can also be explained with similar reasoning using sp^2 orbitals with one lobe directed into the center of the ring.

The above interpretation of the bonding in methylcyclopropene is also consistent with the hybridization[14,15] as determined by the $J_{^{13}\mathrm{CH}}$ spin–spin coupling constants.

The barrier to internal rotation in methylcyclopropene of 1390 cal/mole has decreased significantly from the value of 2000 cal/mole in propylene.[16] However, the barrier in N-methylmethylenimine[17] is nearly identical with the value in propylene which has caused Dale[18] to question the role of the adjacent vinyl proton in giving rise to the origin of the barrier.[19] Lowe[20] has discussed the equal barriers in N-methylmethylenimine and propylene on the basis of an electrostatic model. The methyl barrier goes down when the vinyl proton is removed, but it also goes up when the angle between the double bond and the methyl rotor axis decreases as in N-methylmethylenimine. According to Lowe, these two compensating factors lead to nearly equal barriers in the two molecules.

In 1-methylcyclopropene we have removed the adjacent proton as in N-methylmethylenimine and we have also increased the double bond–methyl rotor axis angle. Extending Lowe's arguments to this molecule gives the required lowering of the barrier. However, there are other arguments which indicate the electrostatic model may not be the most valuable approach in understanding the origin to the barrier to internal rotation.[19,21]

We are continuing our work on 1-methylcyclopropene in order to determine V_6 and the conformation of the methyl group. These data ought to lead to a better understanding of the bonding and origin to the barrier in small-ring compounds.

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

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(13) See W. H. Flygare and V. W. Weiss, *J. Chem. Phys.*, **45**, 2785 (1960), for further details in the construction of these hybrid orbitals.

(14) C. Juan and H. S. Gutowsky, *ibid.*, 37, 2198 (1962), and references cited therein.

(15) G. L. Gloss and R. B. Larrabee, *Tetrahedron Letters*, 287 (1965).

(16) E. Hirota, *J. Chem. Phys.*, **45**, 1984 (1966).

(17) K. V. L. N. Sastry and R. F. Curl, *ibid.*, **41**, 77 (1964).

(18) J. Dale, *Tetrahedron*, **22**, 3373 (1966).

(19) For a discussion of recent data in light of theories on the origin of the barrier, see W. H. Flygare, *Ann. Rev. Phys. Chem.*, in press.

(20) J. P. Lowe, *J. Chem. Phys.*, **45**, 3059 (1966).

(21) W. H. Fink and L. C. Allen, *ibid.*, **46**, 2261 (1967).

(22) (a) C. S. Marvel Fellow; (b) Alfred P. Sloan Fellow.

M. K. Kemp,[22a] **W. H. Flygare**[22b]
W. A. Noyes Chemical Laboratory
University of Illinois, Urbana, Illinois

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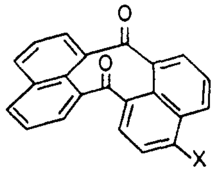
Preparation and Racemization of an Optically Active 1,8-(1′,8′-Naphthalyl)naphthalene[1]

Sir:

We have previously pointed out that in 1,8-(1′,8′-naphthalyl)naphthalene (**1**) simultaneous conrotation or disrotation[2] of the carbonyl groups about the carbon–carbon single bonds is inhibited by the considerable angle strain it introduces, and that a suitably substituted derivative of **1** consequently might be obtained optically active.[3] We now report the preparation of optically active 4-nitro-1,8-(1′,8′-naphthalyl)naphthalene (**2**) and the kinetics of racemization of this new dissymmetric system. The conformational stability of **2** is such that it racemizes on standing in chloroform solution at 25.5° with a half-life of 102 min.



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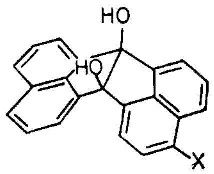
2, X = NO$_2$



3, X = H
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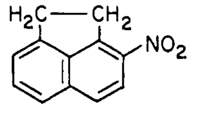

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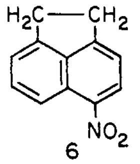

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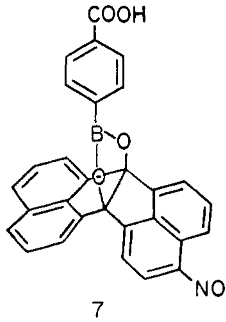

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Nitration of glycol **3**[4] either with nitric acid in a mixture of acetic acid and nitromethane or with nitryl tetrafluoroborate[5] in nitromethane–acetonitrile solution gave the nitroglycol **4**.[6] The position of nitration follows from the known reactions of acenaphthene[7,8] and was substantiated by comparison of the nuclear magnetic resonance spectra of **4**, the derived diacetate,[6] and the derived acetonide[6] with the spectra of both 3-nitroacenaphthene (**5**)[7] and 5-nitroacenaphthene (**6**).[8] Reaction of the nitroglycol **4** with a slight excess of *p*-boronobenzoic acid[9] in refluxing benzene using a water separator furnished the cyclic boronate ester carboxylic acid **7**.[6] This esterification provided convenient access to a derivative of **4** suitable for optical resolution; the

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(1) This investigation was supported by National Science Foundation Grant GB-137 and National Institutes of Health Grant AM-02493.

(2) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395 (1965).

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(6) This new substance gave acceptable elemental analyses for carbon, hydrogen, and nitrogen.

(7) 3-Nitroacenaphthene (**5**) is available in low yield by nitration of acenaphthene with acetyl or benzoyl nitrate in petroleum ether: G. T. Morgan and H. A. Harrison, *J. Soc. Chem. Ind.* (London), **49**, 413T (1930).

(8) Direct nitration of acenaphthene under a variety of conditions gives 5-nitroacenaphthene (**6**) in good yield: F. Sachs and G. Mosebach, *Ber.*, **44**, 2852 (1911).

(9) A. Michaelis, *Ann.*, **315**, 19 (1901).