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Recently there has been a renewed interest in the effect of substituents upon the C–C bond lengths in cyclopropyl derivatives. Penn and Boggs[1] showed for a rather extensive series of such molecules that unsaturated substituents led to a shortening of the bond opposite the substituent (the C_2–C_3 bond) of approximately 0.015 Å compared to cyclopropyl species having saturated substituents. This result agreed with Hoffmann's[2] theoretical suggestion that a good π-electron acceptor substituent should lead to a delocalization of electron density out of the ring via the substituent's interaction with the highest occupied ring molecular orbital ($3e'$). Since the appropriate member of this degenerate pair is C_1–C_2 (and C_1–C_3) bonding and C_2–C_3 antibonding,[2] the predicted result is a shortening of C_2–C_3 and a lengthening of the adjacent (C_1–C_2 and C_1–C_3) bonds. The recent microwave study of Pearson *et al.*[3] on cyclopropyl cyanide led to C_1–$C_2 = 1.529$ Å and C_2–$C_3 = 1.500$ Å, in complete agreement with the theoretical prediction.

The situation with saturated substituents is not so clear. The analysis of Penn and Boggs suggests that such substituents leave the C_2–C_3 bond at essentially the parent cyclopropane distance (1.510 Å).[4] The precise substitution structure of cyclopropyl chloride[5] agrees with this observation, since C_2–$C_3 = 1.515$ Å and C_1–$C_2 = 1.513$ Å. On the other hand, Peretta and Laurie[6] recently reported that C_2–$C_3 = 1.553$ Å and C_1–$C_2 = 1.464$ Å for 1,1-difluorocyclopropane.

Some years ago we reported[7] the microwave spectrum and conformation (C_s symmetry) of cyclopropylamine, another example of a molecule with a saturated substituent. At that time no C^{13} data were reported, although unpublished data[8] were available for the 2-^{13}C c-type Q-branch lines. Consequently a precise ring structure was not reported. In this study we report the microwave spectra of the C^{13} species and the cyclopropyl ring substitution structure.

Table I presents the observed natural abundance spectra for the 1-^{13}C and 2-^{13}C species. The transitions showed the expected ^{14}N hyperfine structure, which was satisfactorily described by the coupling constants of the normal isotopic species.[9] We have reported in Table I only the hypothetical ν_0 values, which represent the centers of gravity of the hyperfine multiplets. The line intensities were at the expected 1% level, with the 2-^{13}C species having twice the intensity of the 1-^{13}C species because of the two equivalent 2-^{13}C positions. Great care was taken to sort out interfering lines and Stark components from the parent compound and from ammonia, which was invariably present as an impurity. All data were obtained using high-sensitivity

stabilized runs, in some cases with full computer control.[10]

Analysis of the Table I data led to the following rotational constants in MHz for the 1-^{13}C species: $A = 16\,141.97 \pm 0.02$, $B = 6696.09 \pm 0.01$, $C = 5790.81 \pm 0.01$; and for the 2-^{13}C species: $A = 15\,976.83 \pm 0.03$, $B = 6645.05 \pm 0.01$, $C = 5702.48 \pm 0.01$. The uncertainties represent the standard deviations, and the goodness of fit is seen from the calculated minus observed values in Table I.

Using these newly determined rotational constants along with those reported earlier[7] for the normal species, the principal axis r_s coordinates of the carbon atoms were found by the use of Kraitchman's equations[11] to have the following values in Angstroms: $a_1 = 0.250$, $b_1 = 0$, $c_1 = -0.494$, $a_2 = a_3 = -0.931$, $b_2 = -b_3 = 0.756$, $c_2 = c_3 = 0.131$. The experimental (statistical) uncertainty of these values is 0.001 Å or less in all cases. From these results the C_1–C_2 (C_1–C_3) and C_2–C_3 bond lengths are computed to be 1.535 ± 0.006 and 1.513 ± 0.003 Å, respectively. The listed uncertainties account for the effects of vibration–rotation interaction in addition to the experimental precision, and have been estimated by a previously reported method.[10] The purely experimental uncertainties contribute less than ± 0.002 Å to the total.

The results of this study and those for the previously mentioned chloro- and difluoro-cyclopropane studies do not suggest a clearly definable pattern of behavior for the saturated substituents. If the substituent were a good electron *donor* whose highest filled orbital was of the proper symmetry, electron density might be transferred into one of the lowest unoccupied cyclopropyl molecular orbitals.[12] In the case of the $1a_2'$ (totally C–C antibonding) orbital such delocalization would lead to lengthening of all bonds. On the other hand, inter-

TABLE I. Cyclopropylamine 1-^{13}C and 2-^{13}C transitions (in MHz).

Transition	1-^{13}C ν_0(obs)[a]	ν_0(obs)-ν_0(calc)	2-^{13}C ν_0(obs)[a]	ν_0(obs)-ν_0(calc)
$3_{12} \rightarrow 3_{22}$			26 625.47	−0.06
$4_{13} \rightarrow 4_{23}$	25 293.42	0.08	24 832.82	−0.03
$5_{14} \rightarrow 5_{24}$	23 192.53	−0.01		
$6_{15} \rightarrow 6_{25}$	20 770.98	−0.06	20 154.72	0.08
$7_{16} \rightarrow 7_{26}$	18 107.47	0.01		
$0_{00} \rightarrow 1_{10}$	22 838.02	−0.04	22 621.84	−0.04
$1_{01} \rightarrow 2_{11}$	36 230.23	−0.01	35 192.07	0.08
$2_{11} \rightarrow 3_{03}$			25 488.81	0.08
$3_{12} \rightarrow 4_{04}$	36 462.14	−0.02	35 808.03	−0.09

[a]Uncertainty estimated to be less than ± 0.1 MHz.

action of the substituent with the appropriate $4e'$ orbital would lead to a decrease in C_2–C_3 and an increase in C_1–C_2.

For the halogen substituents, both of these donor mechanisms are possible by virtue of the atomic lone pairs. The experimental result for the chloro molecule is rather neutral, while that for the difluoro species (in particular, the short C_1–C_2 bond) seems at variance with the simple predictions. In the amino case, the lone pair orbital is symmetrical with respect to the molecular symmetry plane, and consequently only the interaction with the $4e'$ orbital is possible. This mechanism is satisfied by our results for the C_1–C_2 bond length while that for the C_2–C_3 bond is rather inconclusive. Thus it appears that the effects of saturated substituents are not as clearly describable as are those of the unsaturated substituents.

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Radiationless deactivation rates of the lowest triplet state of tetraphenylporphin at 2°K[*]

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Prompted by an interest in radiationless transitions in large planar aromatic molecules we have measured the depopulation rates for the spin sublevels of the lowest triplet state of α, β, γ, δ tetraphenylporphin (TPP) in n-octane at 2°K, using optical detection of magnetic resonance. Three sharp zero-field EPR transitions at 502, 839, and 1341 MHz were observed for TPP as microwave-induced changes in the fluorescence intensity at a wavelength of 652 nm. The fluorescence of TPP in polycrystalline n-octane was excited by the 514.5 nm line of a Spectra-Physics model 164 argon ion laser. All three observed zero-field triplet state EPR transitions corresponded to increased fluorescence intensity at 652 nm with linewidths on the order of 5–10 MHz. The fine structure parameters calculated from the zero-field transition energies are $|D| = 0.0363 \pm 0.0002$ cm^{-1}, $|E| = 0.0083 \pm 0.0002$ cm^{-1}, in agreement with the high-field EPR results for TPP in 1:1 ether-ethanol glasses at 100°K.[1]

To measure the depopulation rates for the triplet state spin sublevels the time-dependent response of the fluorescence (at 652 nm) to a modulated saturating microwave field was measured for the observed zero-field transitions.[2] Figure 1 gives the results of these

experiments; all measured curves plotted in Fig. 1 were checked to be independent of incident laser power. Using methods of calculation described previously,[2] the depopulation rate constants for the triplet spin sublevels were determined to be $k_x = 168 \pm 40$ sec^{-1}, $k_y = 692 \pm 50$ sec^{-1}, $k_z = 50 \pm 10$ sec^{-1}, where the designations x, y, and z refer to the top, middle, and lowest spin sublevels, consistent with the porphyrin principal axis scheme adopted by van der Waals et al.[3,4]

Since it is known from the work of Gradyushko et al. that the depopulation of the TPP triplet state is dominated by nonradiative deactivation,[5] the rate constants measured here represent the rates of radiationless decay for the individual spin sublevels of the photoexcited triplet state. The middle (y) spin level is the most active in the triplet state $T_1 \rightarrow S_0$ intersystem crossing in TPP, and the relative magnitude of spin sublevel decay, $k_y > k_x > k_z$, is the same as has been found for porphin free base[4] and for the triplet states of chlorophyll a and b,[2] suggesting common modes of deactivation for these similar π-electron systems. These results differ from rates measured for the triplet state of Zn porphin, whose deactivation is primarily through the lowest (z) spin level and whose rates are presumably strongly