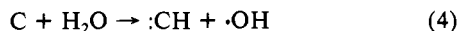


ventional radical chemistry, open-shell states are predicted to prefer abstraction while closed shells should insert. However, in the reaction between carbon and water, the abstraction route (eq 4)



is thermodynamically unfavorable for both C(¹D) ($\Delta H = 8.2$ kcal/mol) and C(³P) ($\Delta H = 38.2$ kcal/mol). Thus the O-H bond strength appears to preclude abstraction along an open-shell energy surface. Abstractions by carbon are thought to lead to methylene, which, in the present case, is expected to react with water to generate methanol.²⁸ However, a careful search of the products of the C + H₂O reaction does not reveal methanol.

Conclusions

These investigations demonstrate the utility of combining a theoretical and experimental approach to the study of simple but highly reactive species such as carbon. The 3-21G basis is found to be adequate for geometry searches while the MP3/6-31G** basis is flexible enough to give confidence to about 5 kcal/mol

after ZPC effects have been included.

In the reaction between carbon and water, singlet carbon atoms are predicted and observed to be reactive toward water by both insertion and deoxygenation. Triplet carbon atoms are predicted to be unreactive toward water. Oxygen-scavenging experiments confirm this prediction. The O-H bond strength precludes abstraction by both C(¹D) and C(³P) and none is observed. We are currently investigating the reactions of other substrates with carbon from both a theoretical and experimental viewpoint in order to attempt to predict and explain reactivity patterns.

Acknowledgments. We thank the Auburn University Computation Center for a generous allotment of computer time. One of M.L.M. thanks Auburn University for the award of a Grant-in-Aid 82-54. S.N.A. and P.B.S. gratefully acknowledge support of the experimental portion of this research by the National Science Foundation Grant CHE-8103034.

Registry No. Carbon, 7440-44-0; water, 7732-18-5; hydroxymethylene, 19710-56-6.

Microwave Structures of Cyanocyclopropane and Cyclopropylacetylene. Effects of Cyclopropyl π Conjugation on Structure

Marlin D. Harmony,*† R. N. Nandi,† James V. Tietz,† Jong-In Choe,† Stephen J. Getty,† and Stuart W. Staley*†

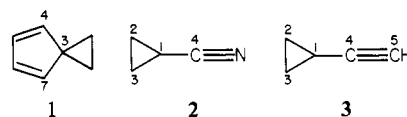
Contribution from the Departments of Chemistry, University of Kansas, Lawrence, Kansas 66045, and University of Nebraska, Lincoln, Nebraska 68588.
Received November 12, 1982

Abstract: Microwave spectra of two isotopic forms of cyanocyclopropane and four isotopic forms of cyclopropylacetylene have been observed and analyzed. When these data were combined with previous measurements, complete heavy-atom substitution structures were determined. Among other parameters, the bond distances (Å) are as follows: for cyanocyclopropane, C₁C₂ = 1.529 ± 0.005, C₂C₃ = 1.500 ± 0.003, C₁C₄ = 1.420 ± 0.006, C₄N = 1.161 ± 0.004; for cyclopropylacetylene, C₁C₂ = 1.527 ± 0.006, C₂C₃ = 1.503 ± 0.007, C₁C₄ = 1.422 ± 0.006, C₄C₅ = 1.211 ± 0.004, C₅H = 1.055 ± 0.003. The structural results have been compared to those in related molecules and are in accord with a simple theoretical model of π -electron donation from the cyclopropane ring to the π systems of the substituents. These data also point to the conclusion that cyclopropyl is a better donor than vinyl when these groups are conjugated with cyano or ethynyl.

Introduction

Structural evidence for the π -conjugative interaction of the cyclopropyl ring has begun to emerge more clearly during the past few years. A recent contribution^{1,2} from our laboratories has shown that the cyclopropyl group in spiro[2.4]hepta-4,6-diene (**1**) enters into effective π conjugation with the diene system. The experimental results are well described by a simple frontier orbital model¹⁻³ (Figure 1) which treats cyclopropyl as a π -electron donor. Allen^{4,5} has recently surveyed a large amount of X-ray diffraction data and his analysis provides strong evidence for the universality of this behavior for various cyclopropyl systems with π -acceptor substituents. The subject has also been addressed theoretically by means of ab initio calculations.^{2,6-8}

In the present study we report the complete heavy-atom structures of two of the simplest molecules for which this cyclopropyl π conjugation is possible, viz., cyanocyclopropane (**2**) and cyclopropylacetylene (**3**). An earlier microwave structural study⁹ of **2** provided ring data but no structural parameters for the cyano (nitrile) group, whereas an NMR study of partially oriented **2** provided the relative proton structure.¹⁰ A microwave study of **3** yielded no reliable structural data,¹¹ and an electron diffraction study that appeared after the present work was underway provided only partly reliable results.¹²



Spectral Samples. Commercially available cyanocyclopropane (Aldrich) was used for spectral surveys of the normal isotopic species and also for some observations of the 1-¹³C and 2-¹³C

- (1) Staley, S. W.; Howard, A. E.; Harmony, M. D.; Mathur, S. N.; Kattija-Ari, M.; Choe, J.-I.; Lind, G. *J. Am. Chem. Soc.* **1980**, *102*, 3639.
- (2) Harmony, M. D.; Mathur, S. N.; Choe, J.-I.; Kattija-Ari, M.; Howard, A. E.; Staley, S. W. *J. Am. Chem. Soc.* **1981**, *103*, 2961.
- (3) Hoffmann, R. *Tetrahedron Lett.* **1970**, 2907.
- (4) Allen, F. H. *Acta Crystallogr., Sect. B* **1980**, *B36*, 81.
- (5) Allen, F. H. *Acta Crystallogr., Sect. B* **1981**, *B37*, 890.
- (6) Skancke, A.; Boggs, J. E. *Acta Chem. Scand., Ser. A* **1978**, *A32*, 893.
- (7) Skancke, A.; Boggs, J. E. *J. Mol. Struct.* **1979**, *51*, 267.
- (8) Oberhammer, H.; Boggs, J. E. *J. Mol. Struct.* **1979**, *57*, 175.
- (9) Pearson, R., Jr.; Choplin, A.; Laurie, V. W. *J. Chem. Phys.* **1975**, *62*, 4859.
- (10) Cole, K. C.; Gilson, D. F. R. *Can. J. Chem.* **1976**, *54*, 2788.
- (11) Collins, M. J.; Britt, C. O.; Boggs, J. E. *J. Chem. Phys.* **1972**, *56*, 4262.
- (12) Klein, A. W.; Schrupf, G. *Acta Chem. Scand. A* **1981**, *35*, 431.
- (13) Allen, C. F. H. "Organic Syntheses", 2nd ed.; Wiley: New York, 1941; Coll. Vol. I, p 156.

*University of Kansas.

†University of Nebraska.



Figure 1. Frontier molecular orbital model for π conjugation in cyanocyclopropane.

Table I. Rotational Constants for Cyanocyclopropane Isotopic Species

	^{13}CN	C^{15}N
<i>A</i>	15776.222 \pm 0.006 ^a	15760.167 \pm 0.005
<i>B</i>	3438.845 \pm 0.001	3359.393 \pm 0.001
<i>C</i>	3263.042 \pm 0.001	3192.080 \pm 0.001
$r_s^{\prime}aaaa$	-0.169 \pm 0.001	-0.165 \pm 0.001
$r_s^{\prime}bbbb$	$-(0.423 \pm 0.002) \times 10^{-2}$	$-(0.406 \pm 0.001) \times 10^{-2}$
$r_s^{\prime}cccc$	$-(0.491 \pm 0.002) \times 10^{-2}$	$-(0.473 \pm 0.002) \times 10^{-2}$
$r_s^{\prime}bbcc$	$-(0.446 \pm 0.002) \times 10^{-2}$	$-(0.429 \pm 0.001) \times 10^{-2}$
$r_s^{\prime}aabb + r_s^{\prime}aacc$	$-(0.966 \pm 0.002) \times 10^{-2}$	$-(0.984 \pm 0.002) \times 10^{-2}$

^a All values in MHz. Uncertainties represent the standard deviations.

natural abundance spectra. Measurements reported here for the ^{15}N and $4\text{-}^{13}\text{C}$ species were performed with samples prepared from 4-chlorobutyronitrile enriched in these isotopes. The latter compounds (^{13}CN or C^{15}N) were prepared¹⁴ from appropriately labeled sodium cyanide (MSD Isotopes). All compounds were purified on a 1-m 18% Carbowax 20M on 100/200 mesh Chromosorb P column at 100–150 °C. All spectral measurements of cyclopropylacetylene were performed by observing the isotopic spectra in their natural abundance with a sample prepared by established procedures.¹⁵

Microwave Spectra. Microwave spectra were obtained with an HP-8460A spectrometer operated in R-band (26.5–40 GHz). Radio frequency-microwave double resonance (RFMDR) measurements were performed by using the methods and apparatus previously described.^{16,17} Sample pressures were normally in the range of 15–30 mtorr, and the waveguide sample cell was operated at room temperature (20–23 °C) and at reduced temperatures (\sim -60 °C) by using dry-ice cooling. Frequency measurements reported in this work are expected to have an accuracy of approximately ± 0.05 MHz or better.

Results

Because spectral assignments had previously been reported for both cyanocyclopropane⁹ and cyclopropylacetylene,¹¹ assignments for the various isotopic species were obtained in a relatively straightforward fashion. For each of the ^{13}C - and ^{15}N -enriched samples of **2**, a total of 36 *a*- and *c*-type transitions, involving a broad variety of selection rules and states, were measured. These spectra, available as supplementary Tables SI and SII, were fit to a standard rotational Hamiltonian model to obtain the rotational and centrifugal distortion constants, which are tabulated in Table I.

In the case of cyclopropylacetylene, the previously reported spectrum of the normal isotopic species yielded a rather imprecise value of the *A* rotational constant (± 35 MHz), since only *a*-type, R-branch lines were observed.¹¹ We attempted to observe *c*-type transitions to obtain an improved fit, but the very small value of μ_c (≤ 0.05 D) prevented this. We were able, however, to observe several high-*J* Q-branch lines which considerably reduced the uncertainty in the *A* rotational constant. The complete list of observed transitions for the normal species of cyclopropylacetylene is available as supplementary Table SIII, and the rotational constants are presented in Table II.

The four monosubstituted ^{13}C species of the acetylene compound were all studied in their natural abundances of 1 or 2%. Consequently, only the *a*-type, R-branch lines could be detected. The

weak spectra were assigned unambiguously, however, by using RFMDR techniques^{16,17} and by careful observation of relative intensities (including temperature dependence). Supplementary Tables SIV–SVII contain the spectral data, and Table II presents the resulting rotational constants. We also include the rotational constants for the $\text{C}\equiv\text{CD}$ isotopic species reported by earlier workers.¹¹ It should be noted that the *B* and *C* constants are well determined for all the isotopic species but that the *A* values are rather imprecise.

Finally, we should mention that the cyanocyclopropane ^{13}CN and C^{15}N isotopic species data are in agreement with less accurate and less extensive unpublished results obtained by Boggs and Penn¹⁸ in natural abundance.

Structures

The new data reported in this study, along with the previously reported work,^{9,11} permit complete high-quality structures to be obtained for the heavy atoms of both cyanocyclopropane and cyclopropylacetylene.

Cyanocyclopropane. Here the quality of the rotational constant data is excellent. Pearson et al.⁹ previously reported the r_s coordinates¹⁹ for the ring carbons, computed by using Kraitchman's equations.²⁰ With the aid of Pearson's data for the normal species and the new data in Table I, we report the r_s coordinates of the cyano group in Table III. Because the cyano atoms lie in a plane of symmetry, the rotational constant data can be analyzed in several ways. This occurs because, in the absence of vibration-rotation interactions

$$\Delta I_a + \Delta I_c = \Delta I_b \quad (1)$$

We find that the various data sets lead to coordinates with very little variation (± 0.001 Å), indicating the high quality of the data and the close adherence of the r_s coordinates to pseudovibrationless behavior. For consistency with the cyclopropylacetylene work, we record in Table III the results obtained by using only the *B* and *C* rotational constant data. On combining our results with those of Pearson et al.,⁹ the complete heavy-atom structure is now available and is tabulated in Table IV.

The uncertainties presented in both Tables III and IV represent the RMS average of the experimental error and the "Costain" error²¹ computed as $\Delta g = 0.0015/g$, $g = a, b, c$. Generally speaking, the Costain error dominates this uncertainty calculation. It should be noted that there are several rather small *c* coordinates, the smallest being that of C_4 (-0.144 Å). Nevertheless, we believe the principal structural results and their uncertainties are accurately prescribed. These small coordinates have only a modest influence upon the in-plane distances, since the *a* axis is more-or-less parallel to the C–CN group. Moreover, the C–CN group is found to be linear within the experimental errors. Incidentally, a change in sign of the small C_4 coordinate would lead to gross nonlinearity as well as inconsistent bond lengths. Overall, the structural parameters summarized in Table IV must be considered to be of high quality, and the uncertainties are, in general, conservative.

Cyclopropylacetylene. The data for the normal species and the 1% ^{13}C isotopic species lead immediately to the r_s coordinates of C_1 , C_4 , and C_5 . Since the *A* rotational constants are imprecisely determined for the isotopic species, we have used only the *B* and *C* rotational constant data in accord with the earlier discussion (see eq 1). The acetylene hydrogen was located similarly by using the previously reported deuterium data.¹¹ Table V summarizes the results of these coordinate calculations.

For the remaining two ring carbons, the standard coordinate computation using the full Kraitchman equations is not reliable because of the poor-quality *A* rotational constant for the 2- ^{13}C species, and the previously used computation based only on *B* and *C* constants is of course not applicable for these atoms. Consequently, we have used the scheme of Nösberger et al.,²² in which

(14) Schlatter, M. J. "Organic Syntheses"; Wiley: New York, 1955; Coll. Vol. III, p 223.

(15) Schoberth, W.; Hanack, M. *Synthesis* **1972**, 703.

(16) Wodarczyk, F. J.; Wilson, E. B. *J. Mol. Spectrosc.* **1971**, 37, 445.

(17) Mathur, S. N.; Harmony, M. D. *J. Mol. Spectrosc.* **1978**, 69, 37.

(18) Boggs, J. E.; Penn, R. E., personal communication.

(19) Costain, C. C. *J. Chem. Phys.* **1958**, 29, 864.

(20) Kraitchman, J. *Am. J. Phys.* **1952**, 21, 17.

(21) Costain, C. C. *Trans. Am. Crystallogr. Assoc.* **1966**, 2, 157.

Table II. Rotational Constants for Cyclopropylacetylene

	normal	1- ¹³ C	2- ¹³ C	4- ¹³ C	5- ¹³ C	C≡CD ^b
A	15722.90 ± 1.33 ^a	15538.76 ± 36.04	15426.69 ± 23.63	15681.92 ± 23.999	15772.14 ± 21.71	15653 ± 63
B	3360.006 ± 0.004	3350.53 ± 0.02	3319.58 ± 0.02	3334.68 ± 0.02	3254.22 ± 0.02	3139.67 ± 0.01
C	3192.703 ± 0.004	3190.99 ± 0.02	3146.32 ± 0.02	3170.33 ± 0.02	3097.90 ± 0.01	2997.95 ± 0.01

^a All values in MHz; uncertainties are the standard deviations. ^b From ref 11.

Table III. Substitution (r_s) Coordinates of Cyanocyclopropane (Å)^a

atom	a	b	c
C ₁ ^a	-0.2950 ± 0.0051	0	-0.5940 ± 0.0025
C ₂ , C ₃ ^a	-1.3436 ± 0.0011	±0.7500 ± 0.0020	0.2274 ± 0.0066
C ₄	1.0519 ± 0.0014	0	-0.1443 ± 0.0104
N	2.1485 ± 0.0007	0	0.2367 ± 0.0063

^a These values have been recomputed from the B and C rotational constants of ref 9.

Table IV. Structural Parameters (r_s) for Cyanocyclopropane and Cyclopropylacetylene

	cyanocyclopropane	cyclopropylacetylene
C ₁ C ₂	1.529 ± 0.005 ^a	1.527 ± 0.006 ^b
C ₂ C ₃	1.500 ± 0.003	1.503 ± 0.007 ^b
C ₁ C ₄	1.420 ± 0.006	1.422 ± 0.006
C ₄ C ₅		1.211 ± 0.004
CN	1.161 ± 0.004	
C ₃ H		1.055 ± 0.003
∠C ₂ C ₁ C ₄	118.7 ± 0.4	119.3 ± 0.4 ^b
α	179.3 ± 0.7	179.3 ± 0.7
β		179.9 ± 0.7

^a Distances in Å; angles in degrees. Uncertainties are computed from those of Tables III and V and include a standard estimate of zero-point vibration effects. ^b Near- r_s structural parameters computed by assuming CH = 1.080 Å, ∠HCH = 114.6° with local C_{2v} symmetry, and ∠C₄C₁H = 109.5°.

Table V. Substitution (r_s) Coordinates of Cyclopropylacetylene (Å)

atom	a	b	c
C ₁	-0.2930 ± 0.0057	0	-0.5872 ± 0.0078
C ₄	1.0630 ± 0.0015	0	-0.1603 ± 0.0014
C ₅	2.2135 ± 0.0008	0	0.2174 ± 0.0077
H	3.2168 ± 0.0005	0	0.5452 ± 0.0031

coordinates or structural parameters are computed by least-squares fitting of isotopic differences in moments of inertia along with the moments of inertia of the normal species. In our case we eliminate the poor ΔI_a value from the computation and use only ΔI_b and ΔI_c along with I_a , I_b , and I_c for the normal species. We fix the remaining carbon atoms and the acetylene hydrogen at their experimental r_s values and position the ring hydrogens as they have been reported in more complete studies of related molecules.²³ The three structural parameters that locate carbons C₂ and C₃ are then determined by a least-squares fit of the five pieces of data, the parent moments being weighted at 1% of the ΔI_b and ΔI_c values. The resulting structural parameters are summarized in Table IV. The reported uncertainties have been computed in the same manner as described for the cyano compound, that is, they include experimental plus Costain uncertainties.

The method of Nösberger et al.²² maintains the spirit of Costain's r_s coordinates; i.e., it is expected to lead to effective cancellation of zero-point vibration effects. For those molecules where reliable data are available for a complete r_s calculation, the two methods lead to very similar results.²² Moreover, because of the heavy reliance upon isotopic difference data, partial or incomplete structures may be obtained with relative insensitivity to the unknown atomic positions or structural parameters. In the

present case, we have varied the unknown CH distances and CCH angles by ±0.005 Å and ±2°, respectively, in order to assess the validity of the heavy-atom structure. These tests show that the heavy-atom structural parameters remain within the listed uncertainties of Table IV. Therefore, in the absence of very unusual ring-hydrogen parameters, the cyclopropylacetylene heavy-atom ring structure is expected to be of comparable quality to a true r_s structure. In Table IV we have identified the structural parameters involving C₂ and C₃ as being "near r_s ".

Discussion

The new experimental data reported here along with previously available data have led to complete high-quality structures of the heavy atoms of cyanocyclopropane and cyclopropylacetylene. These molecules are especially interesting in the context of the behavior of the cyclopropyl ring as a π -electron donor. This subject has been discussed previously in some detail,^{2,4,5,7} and a rather large amount of data confirms the simple frontier orbital model¹⁻³ (Figure 1) for acceptor-substituted cyclopropanes which predicts that the C₁C₂ bond should become longer than in cyclopropane, while the C₂C₃ bond should become shorter. Note from Table IV that the subject molecules of this study satisfy this prescription completely.

It is of interest to compare the relative acceptor abilities of the ethynyl and cyano groups. According to Figure 1, the degree of distortion of the cyclopropyl ring from an equilateral triangle should provide a measure of the acceptor ability of the substituent. As seen in Table IV, the cyclopropyl rings of **2** and **3** are significantly and similarly distorted, although to a somewhat lesser degree than in spiro[2.4]hepta-4,6-diene (**1**).² Interestingly, the lengthening of C₁C₂ and C₁C₃ is approximately twice as great as the shortening of C₂C₃ (relative to the cyclopropane value of 1.510 Å)²⁴ in three compounds. This is in qualitative accord with a simple frontier molecular orbital model (Figure 1) since the p orbital contribution at C₁ is twice as large as that at C₂ or C₃.

The following facts suggest that cyano should be a better acceptor group than ethynyl. (a) Cyano has a greater σ_p^- value ($\sigma_p^- = 0.88-1.02$) than does ethynyl ($\sigma_p^- = 0.52$).²⁵ (b) The electron affinity for HCN (-2.26 eV)²⁶ is greater than that of acetylene (-2.6 eV),²⁷ as measured by electron transmission spectroscopy. (c) The p orbital coefficient at C₄ in π^* of the triple bond is greater in **2** than in **3**.²⁸ The data in Table IV indeed suggest that the three-membered ring in **2** is slightly more distorted than that in **3**. However, the differences are within experimental uncertainty and these parameters do not by themselves provide proof of the greater acceptor ability of the cyano group.

A feature that is much less well established than the ring behavior is whether the effects of the π -electron delocalization in such systems appear in the structural parameters of the acceptor groups and, if so, whether they provide any clues regarding the donor strength of the cyclopropyl group. In a recent study of **1**,² the cyclopentadiene ring was found to have responded entirely in accord with its π -electron acceptor properties. For the molecules of this study, the frontier orbital model would suggest that the triple bonds should increase in length (compared to a nonconjugated situation) due to an increased electron population in the appropriate π^* orbital. Moreover, the π conjugation should lead

(24) Bastiansen, O.; Fritsch, F. N.; Hedberg, K. *Acta Crystallogr.* **1964**, *17*, 538.

(25) Exner, O. In "Correlation Analysis in Chemistry"; Chapman, N. B., Shorter, J., Ed.; Plenum Press: New York, 1978; pp 484-485.

(26) Howard, A. E., personal communication.

(27) Jordan, K. D.; Burrow, P. D. *Acc. Chem. Res.* **1978**, *11*, 341.

(28) Cf. Jorgensen, W. L.; Salem, L. "The Organic Chemist's Book of Orbitals"; Academic Press: New York, 1973; pp 73-77, 116-119.

(22) Nösberger, P.; Bauder, A.; Günthard, Hs. H. *Chem. Phys.* **1973**, *1*, 418.

(23) Schwendeman, R. H.; Jacobs, G. D.; Krigas, T. M. *J. Chem. Phys.* **1964**, *40*, 1022.

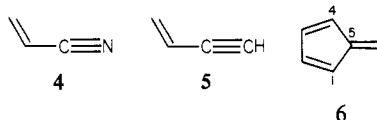
Table VI. Structural Parameters in Related Molecules^a

molecule	C≡N	C=C	C-C ^b
C ₂ H ₂		1.207	
C ₁ C≡CH		1.204	
FC≡CH		1.198	
CH ₃ C≡CH		1.206	1.459
HC≡CCH=O		1.209	1.444
HC≡CC≡N	1.159	1.205	1.378
H ₂ C=CHC≡N (4)	1.164		1.426
H ₂ C=CHC≡N ^c (4)	1.167		1.438
H ₂ C=CHC≡CH ^d (5)		1.215	1.434
FCN	1.159		
HCN	1.155		
CH ₃ CN	1.157		1.458
C ₂ H ₅ CN	1.159		1.459
c-C ₃ H ₅ C≡N ^e (2)	1.161		1.420
c-C ₃ H ₅ C≡CH ^e (3)		1.211	1.422

^a All structures are microwave structures except as noted. See Harmony, M. D.; Laurie, V. W.; Kuczkowski, R. L.; Schwendeman, R. H.; Ramsay, D. A.; Lovas, F. J.; Lafferty, W. J.; Maki, A. G. *J. Phys. Chem. Ref. Data* 1979, 8, 619. ^b Single bond adjacent to triple bond. ^c Combined microwave-electron diffraction data; see: Fukuyama, T.; Kuchitsu, K. *J. Mol. Struct.* 1970, 5, 131. ^d Combined microwave-electron diffraction data; see: Fukuyama, T.; Kuchitsu, K.; Morino, Y. *Bull. Chem. Soc. Jpn.* 1969, 42, 379. ^e This study.

to a shortening of the C₁C₄ single bond. Of course, the effect upon the very strong triple bonds may be only very small.

In addition to the π -conjugation effects, one must consider the effect of a given substituent on the σ components of the bonds under consideration. For comparison purposes, if we take the substituent σ -bonding orbitals of methyl, cyclopropyl, and vinyl to be sp³, sp^{2.2} (see, e.g., Allen⁵), and sp², respectively, then we would expect the σ -bond contribution to cause the CC single bond lengths to vary in the order CH₃CN > 2 > 4 and CH₃C≡CH > 3 > 5. At the same time, Bent's empirical rule²⁹ would predict



that the adjacent triple bond lengths in the same molecules should vary as CH₃C≡CH < 3 < 5 due to the σ -bond changes. If cyclopropyl is a better donor than vinyl, the previously mentioned π conjugation should lead to the ordering CH₃CN > 4 > 2 and CH₃CH > 5 > 3 for the single bonds and CH₃CN < 4 < 2 and CH₃C≡CH < 5 < 3 for the triple bonds. For cases where vinyl is a better π donor, 4 and 2 and 5 and 3 interchange in the latter inequalities.

From the data of Table VI it is clear that there is not much variation in the triple bond lengths, particularly for the CN group. For the C≡N and C=C groups one might consider the methyl- or ethyl-substituted molecules as representing the essentially pure unconjugated triple bonds. Then one observes that the C≡N and C=C bond lengths have increased slightly in the order CH₃CN < 2 < 4 and CH₃C≡CH < 3 < 5, which is precisely the ordering predicted for dominant σ -bond effects or for π -bond effects with vinyl being the better donor. Unfortunately, the variations are small and within the experimental uncertainties. We can conclude that the C≡N and C=C bonds in the cyclopropyl molecules behave in a manner which is not at variance with the simple frontier orbital model, but it is not possible to draw any conclusions regarding the relative donor abilities of cyclopropyl and vinyl on the basis of these data.

In contrast, the effect of π conjugation upon the intervening single bond can be shown to be significant. Note first that the C-C bonds adjacent to the C≡N or C=C groups in the methyl or ethyl compound are remarkably constant at about 1.459 Å. All of the conjugated π systems show substantially shortened CC

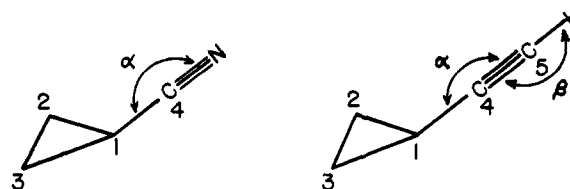


Figure 2. Cyanocyclopropane and cyclopropylacetylene parameter identifications.

single bonds in the order CH₃CN > 4 > 2 and CH₃C≡CH > 5 > 3. (The uncertainty in the latter inequality stems from the fact that a combined electron diffraction-microwave structure for 5 is being compared with microwave-only structures for CH₃C≡CH and 3.) Thus the order for the cyano and the acetylene compounds is *not* consistent with dominant σ -bond hybridization effects and is consistent with the frontier orbital model *only if cyclopropyl is a better π -conjugating group than vinyl in these compounds*. A similar conclusion applies in the comparison of 1 with fulvene (6) where the C orbital hybridizations are essentially identical ($\angle C_4C_3C_7 = 107.0^\circ$ in 1² and $\angle C_1C_5C_4 = 106.8^\circ$ in 6)³⁰ while C₃C₄ is shorter in 1 (1.462 Å)² than is the equivalent bond (C₁C₅) in 6 (1.468 Å).³⁰ Thus the available microwave data provide strong structural evidence for cyclopropyl being a better π -conjugating group than vinyl under certain circumstances. The definition of such circumstances represents an important problem in structural chemistry.

Overall, it seems fair to conclude that the heavy-atom distances in cyanocyclopropane and cyclopropylacetylene offer dramatic substantiation of the π -donor behavior of the cyclopropyl ring. It is interesting also to compare the experimental results of this study with other studies of the same systems. Skancke and Boggs⁷ have determined the ab initio structure of cyanocyclopropane by (nearly) complete geometry optimization in a 4-21G basis. Their values of C₁C₂, C₂C₃, C₁C₄, and CN are respectively 1.525, 1.505, 1.45, and 1.139 Å. The agreement with our data is reasonably good, although the computed C≡N distance is much too short and the C₁C₄ bond is somewhat too long. The computed value of α (see Figure 2) is 179.5°, in excellent agreement with the experimental result in Table IV.

Recently, as this work was in preparation for publication, Klein et al.¹² reported an electron diffraction structure for cyclopropylacetylene. These workers could not distinguish differences in ring CC distances but report $(CC)_{av} = 1.510$ Å, C₁C₄ = 1.440 Å, and C₄C₅ = 1.208 Å. The disagreement of their single bond values with ours is substantial and most likely reflects the previously observed difficulty in determining as many as three unique CC single bond lengths from electron diffraction data.^{2,31} It should be noted that the average CC single bond length (averaged over all *four* single bonds) is 1.493 Å from the diffraction data and 1.495 Å from the microwave data. Thus it appears that the diffraction data have, as in other cases, failed to partition the scattered intensity appropriately among the different bonds.

In a recent analysis of literature data for cyanocyclopropane and vinyl nitrile substructures determined by X-ray crystallography, Allen obtains an average of 1.441 ± 0.004 Å for C₁C₄ in 2 substructures and 1.428 ± 0.003 Å in 4 substructures.⁵ This suggests rather unambiguously that the vinyl group is a much better π -electron donor than cyclopropyl. We believe, however, that these data must be viewed with some degree of skepticism, since the quoted crystallographic C₁C₄ value with its uncertainty does not encompass the value we report for the *simplest* member of the class. It seems likely that other factors must be affecting this bond length in the much more complicated molecules involved in the X-ray data compilation. In the same vein, we believe that the recent conclusion³² (based on thermochemical data) that

(30) Baron, P. A.; Brown, R. D.; Burden, F. R.; Domaille, P. J.; Kent, J. E. *J. Mol. Spectrosc.* 1972, 43, 401. Suenram, R. D.; Harmony, M. D. *J. Chem. Phys.*, 1973, 58, 5842.

(31) Wang, C. S.; Harmony, M. D. *J. Am. Chem. Soc.* 1976, 98, 1108. Suenram, R. D.; Harmony, M. D. *J. Chem. Phys.* 1972, 56, 3837.

(29) Bent, H. A. *Chem. Rev.* 1961, 61, 275.

cyclopropylbenzene has a greater stabilization energy than cyanocyclopropane should also receive closer scrutiny.

Acknowledgment. Research at the University of Kansas has been supported by NSF Grants CHE 78-01118 and CHE 81-16131 and at the University of Nebraska by NSF Grants CHE 78-12218 and CHE 81-10428. Computations were performed at the University of Kansas Academic Computing Center with

(32) Fuchs, R.; Hallman, J. H.; Perlman, M. O. *Can. J. Chem.* **1982**, *60*, 1832.

an allocation of University funds. We are especially grateful to Professor Boggs for discussing his unpublished data with us and to Allison Howard for preparing samples of cyclopropylacetylene.

Registry No. 2, 5500-21-0; 2-¹³CN, 16637-46-0; 2-C¹⁵N, 85267-42-1; 3, 6746-94-7; 3-1-¹³C, 85267-43-2; 3-2-¹³C, 85267-44-3; 3-4-¹³C, 85267-45-4; 3-5-¹³C, 85267-46-5.

Supplementary Material Available: Tables SI-SVII present complete listings of the observed isotopic spectra of the subject molecules (7 pages). Ordering information is given on any current masthead page.

Photoreactivity of Surfactant Ketones as a Probe of the Microenvironment of Organized Media¹

Joseph R. Winkle, Paul R. Worsham, Kirk S. Schanze, and David G. Whitten*

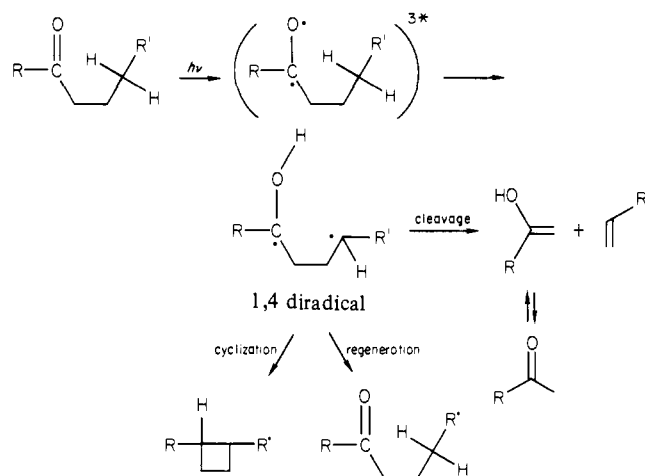
Contribution from the Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514. Received September 16, 1982

Abstract: The Norrish type II photoprocess of surfactant keto acids has been used to examine the relative environment of the ketones in certain organized media. Values for ϕ of 0.81 in SDS micelles and 0.72 in CTAC micelles were obtained for **1**, which are intermediate between the value of 0.29 in benzene and 1.0 in *tert*-butyl alcohol. The ketone thus experiences a fairly hydrophilic environment in micelles. Addition of heptanol to SDS micelles containing **2** causes a decrease in ϕ_{II} values, suggesting that a more hydrophobic region is seen by the ketone, possibly owing to water expulsion from the micelle. Incorporation of **1** into dioctadecylmethylammonium chloride (DODAC) vesicles on irradiation gives values similar to those of a benzene-like medium below the phase-transition temperature, and the ϕ_{II} values slowly increase as the temperature increases. Multilayer assemblies of **1** exhibit very little type II reactivity when irradiated, having values $\phi < 0.01$. The close packing of the molecules which prevents the proper six-membered transition-state geometry to be reached can explain the very low ϕ_{II} .

The ability of carbonyl compounds possessing γ C-H bonds to undergo photochemical intramolecular hydrogen atom abstraction has been well documented.²⁻⁵ It has been found that in the case of aromatic ketones the type II reaction occurs exclusively from the n,π^* triplet state. As shown in Scheme I, upon excitation of the ketone, formation of a 1,4-diradical occurs by hydrogen atom abstraction via a six-membered transition state. The 1,4-diradical may then undergo one of three possible reactions. It can cleave to form the enol of a methyl ketone and an olefin, cyclize to a cyclobutanol derivative, or merely revert back to starting material.

The type II process has been well studied from a photophysical as well as a chemical standpoint. Scaiano and Wagner⁶ have studied the kinetics and lifetimes of the triplet state and the intermediate biradical for a variety of aromatic ketones. In general, the triplet lifetimes are somewhat shorter than the biradical lifetimes, with triplet lifetimes being between 5 and 30 ns for valerophenone and substituted valerophenones in methanol, whereas the biradical values are all about 100 ns in the same

Scheme I



solvent. Biradical and triplet lifetimes for butyrophenone, however, are somewhat higher, on the order of 150 ns in methanol.

Inductive effects, steric factors, and substituent effects have all been examined for the reaction, and it has also been found that a solvent dependency on the quantum yield (ϕ_{II}) occurs for most aromatic ketones.⁷ *n*-Butyrophenone, for example, has a ϕ_{II} in *tert*-butyl alcohol of 1.0 but only 0.3 in benzene. It has been

(1) Photochemical Reactivity in Organized Assemblies 32. A preliminary account of a portion of this work has appeared (ref 10).

(2) Wagner, P. J.; Kelso, P. A.; Zepp, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 7480.

(3) For a review, see: Wagner, P. J. *Acc. Chem. Res.* **1971**, *4*, 168, and references therein.

(4) Lewis, F. D.; Johnson, R. W.; Kory, D. R. *J. Am. Chem. Soc.* **1974**, *96*, 6100.

(5) Wagner, P. J. *Pure Appl. Chem.* **1977**, *49*, 259.

(6) (a) Small, R. D.; Scaiano, J. C. *J. Phys. Chem.* **1977**, *81*, 2126. (b) Small, R. D.; Scaiano, J. C. *Ibid.* **1977**, *81*, 828. (c) Wagner, P. J.; Kempainen, A. E. *J. Am. Chem. Soc.* **1972**, *94*, 7495.

(7) Wagner, P. J. *J. Am. Chem. Soc.* **1967**, *89*, 5898. Wagner, P. J.; Kelso, P. A.; Kempainen, A. E.; McGrath, J. M.; Schott, H. N.; Zepp, R. G. *Ibid.* **1972**, *94*, 7506.