colored (yellowish green) solution. Care was taken in handling the product to maintain the temperature lower than 25 °C.

To examine the course of reduction spectroscopically, the reaction flask was equipped with cells for ESR and absorption measurements connected with/through an intervening sintered glass filter. During the reduction, the ESR and absorption spectra were measured periodically after filtration.

Instrumentation. UV–vis spectra were measured on a Cary Model 14 spectrophotometer, ESR spectra were recorded on a Varian Model E-109E EPR spectrometer, and NMR spectra were recorded on a JEOL 90Q NMR spectrometer. The ^1H off-resonance decoupling and INEPT techniques were used to analyze ^{13}C NMR spectra. Irradiations were carried out with a Ushio 500-W xenon lamp and Toshiba filters.

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Structure of 3-Cyanocyclopropene by Microwave Spectroscopy and ab Initio Molecular Orbital Calculations. Evidence for Substituent–Ring Double-Bond Interactions

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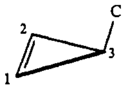
Abstract: A high-quality least-squares molecular structure has been obtained for 3-cyanocyclopropene by microwave spectroscopy. Comparison of the experimental bond lengths ($r(C_1C_2) = 1.292$ Å; $r(C_1C_3) = 1.511$ Å; $r(C_3C_4) = 1.453$ Å) with those of the corresponding bonds in cyclopropene and cyanocyclopropane indicates that some factor is present in addition to the $3b_1$ cyclopropyl (HOMO) $\rightarrow \pi^*$ cyano (LUMO) interaction believed to contribute to the latter compound. These differences are attributed to a decrease in four-electron repulsive interactions ($2b_2$ (cyclopropenyl π) $\leftrightarrow \sigma$ (C–CN)) and an increase in two-electron stabilizing interactions ($2b_2$ (cyclopropenyl) $\pi \rightarrow \sigma^*$ (C–CN)) relative to cyclopropene. Geometry-optimized ab initio molecular orbital calculations at the 6-31G* level support the experimental structural differences and the foregoing conclusions. In particular, the calculated molecular energies suggest that substitution of a cyano group at C_3 of cyclopropene is approximately 1 kcal/mol more stabilizing than substitution on cyclopropane.

In contrast to the extensive and growing literature concerning the influence of substituents on the structure and stability of the cyclopropyl ring, relatively little is known about the corresponding effects on the cyclopropenyl ring. The latter is potentially a fascinating group. For example, Komendantov et al. have determined the Hammett σ_p constant for the 2,3-diphenylcycloprop-2-enyl group to be −0.52, or over twice as large in an absolute sense as that for the *trans*-2,3-diphenylcyclopropyl group (−0.24).[1] As these authors pointed out, this means that the former group is one of the strongest known organic electron-donating groups. Similar, albeit smaller, relative donor effects have also been observed in kinetic studies of solvolysis reactions.[2]

The possibility of σ-electron withdrawal from the cyclopropenyl ring to generate cyclopropenyl cation character was proposed by Greenberg et al.[3] on the basis of calculated relative heats of reaction and by Lien and Hopkinson[4] on the basis of calculated relative strain energies. Although these are certainly reasonable suggestions, it can be extremely difficult to establish a contribution from specific orbitals (in this case, the double bond π orbitals) on the basis of relative total molecular energies. In contrast, high-quality structural studies can provide key information concerning the effects of specific orbitals.

A number of single-crystal X-ray molecular structures are available for highly substituted cyclopropenes, but only a few gas-phase microwave and electron diffraction structures have been reported for simple systems.[5] Allen[5a] has attributed the observation that geminate difluoro substitution shortens the adjacent single bond significantly more in cyclopropene than in cyclopropane to improved $\sigma(1,3)$ overlap in 3,3-difluorocyclopropene, while Domnin et al.[6] have concluded that the available bond length data indicate that cyclopropenium ion character in substituted cyclopropenes appears to be of minor importance. Thus, recent conclusions regarding this problem are contradictory.

In a program to elucidate the precise nature of the effects of substituents upon the structure of the cyclopropyl ring, we have recently reported several microwave and ab initio computational studies of geometric and electronic structures for a variety of simple cyclopropyl species.[7-10] As an aid to understanding the structural and electronic effects of substituents which serve as π-electron acceptors from the cyclopropane ring, and to begin extending our knowledge to the cyclopropene ring, we recently reported a microwave study of the normal isotopic species of 3-cyanocyclopropene (**1**).[11] This work provided dipole moment



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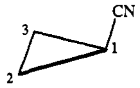

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Table I. Microwave Spectra of 1-^{13}C, 4-^{13}C, and 3-D Isotopic Species^a

transition	obsd ν	C.D.^{b}	dev.^{c}	transition	obsd ν	C.D.^{b}	dev.^{c}
			1-^{13}C				
$4_{04} \leftarrow 3_{03}$	27 380.91	−0.33	−0.04	$5_{05} \leftarrow 4_{04}$	34 220.87	−0.64	0.00
$4_{14} \leftarrow 3_{13}$	27 144.59	−0.29	−0.01	$5_{15} \leftarrow 4_{14}$	33 929.24	−0.61	−0.01
$4_{13} \leftarrow 3_{12}$	27 628.25	−0.24	−0.05	$5_{14} \leftarrow 4_{13}$	34 533.89	−0.51	0.02
$4_{23} \leftarrow 3_{22}$	27 387.52	−0.08	0.06	$5_{24} \leftarrow 4_{23}$	34 233.29	−0.33	0.04
$4_{22} \leftarrow 3_{21}$	27 394.26	−0.08	0.01	$5_{23} \leftarrow 4_{22}$	34 246.80	−0.31	−0.03
			4-^{13}C				
$4_{04} \leftarrow 3_{03}$	27 598.52	−0.33	−0.05	$5_{05} \leftarrow 4_{04}$	34 493.49	−0.65	−0.04
$4_{14} \leftarrow 3_{13}$	27 375.64	−0.29	0.00	$5_{14} \leftarrow 4_{14}$	34 218.12	−0.62	0.03
$4_{13} \leftarrow 3_{12}$	27 831.18	−0.24	0.04	$5_{24} \leftarrow 4_{23}$	34 504.39	−0.33	−0.02
$4_{23} \leftarrow 3_{22}$	27 604.42	−0.08	0.12	$5_{23} \leftarrow 4_{22}$	34 516.23	−0.33	−0.05
$4_{22} \leftarrow 3_{21}$	27 610.24	−0.08	0.00				
			3-D				
$4_{14} \leftarrow 3_{13}$	27 402.62	−0.29	0.01				
$4_{13} \leftarrow 3_{12}$	27 591.05	−0.24	−0.02				
$5_{14} \leftarrow 4_{13}$	34 488.44	−0.51	0.02				
$5_{15} \leftarrow 4_{14}$	34 252.80	−0.61	−0.01				
$5_{05} \leftarrow 4_{04}$	34 368.76	−0.65	0.00				

^{a}All values in MHz. Observed frequencies are better than ±0.05. ^{b}Centrifugal distortion contribution to observed frequency. ^{c}Dev. = Deviation between hypothetical rigid rotor frequencies and those calculated from Table II constants.

and ^{14}N nuclear electric quadrupole coupling data but was inconclusive about several key structural parameters. In order to investigate possible σ polarization in **1** as a complement to our recent study of the highly π-polarized compound methylenecyclopropene,[12] we report here additional microwave measurements which lead to a complete structure of relatively high precision. The experimental data are compared, discussed, and interpreted in conjunction with complementary ab initio geometry-optimized molecular orbital calculations for **1** and related molecules (**2**–**4**).

Table II. Rotational Constants of 1-^{13}C, 4-^{13}C, and 3-D Isotopic Species^a

	1-^{13}C	4-^{13}C	3-D
A	19569 ± 29^b	19815 ± 58	18195 ± 100
B	3483.966 ± 0.004	3507.539 ± 0.009	3460.718 ± 0.003
C	3363.052 ± 0.004	3393.672 ± 0.008	3413.615 ± 0.003

^{a}All values in MHz. Computed from hypothetical rigid rotor frequencies obtained by subtracting centrifugal distortion contributions from observed frequencies. ^{b}Uncertainties are the standard deviations from the least-squares fit. The *A* rotational constants may deviate by 2- or 3σ.

Experimental Section

Synthesis. 3-Cyanocyclopropene.[13] Dimethyl 3-*anti*-cyano-*exo*-tricyclo[3.2.2.0^{2,4}]nona-6,8-diene-6,7-dicarboxylate (2.0 g, 7.7 mmol)[14] was vaporized at 170–220 °C and pyrolyzed at 400 °C and 20 mtorr over 4 h on a 21-mm-o.d. × 40-cm quartz column packed with 25 cm of quartz chips. Dimethyl phthalate was trapped at room temperature, while the 3-cyanocyclopropene was condensed at −78 °C in 35% yield and then distilled before use. The material was shown to be pure by 360-MHz ^{1}H NMR spectrometry.

3-Cyanocyclopropene-*1*-d_1. 3-Cyanocyclopropene (30 mg) was condensed into an NMR tube (−78 °C) containing a 50:50 mixture of ammonia and ammonia-d_3. The tube was sealed and the temperature was raised to 0 °C for 1 h. The ammonia was then removed under vacuum at −78 °C.

3-Cyanocyclopropene-*3*-d_1. Sodium (0.08 g) was added to a tube containing 11 mL of methanol-d_1. After the sodium had dissolved, 1 g of dimethyl 3-*anti*-cyano-*endo*-tricyclo[3.2.2.0^{2,4}]nona-6,8-diene-6,7-dicarboxylate was added and the tube was closed, heated to 120 °C for 3 h, cooled, and quenched with 2 mL of D_2O. The mixture was extracted with ether, and the organic layer was dried with Na_2SO_4. The solvent was evaporated and the product was purified by recrystallization from 30% ethyl acetate/hexane. The product (50 mg) was then pyrolyzed with an equal weight of the undeuteriated exo compound.

Microwave Spectra. Stark modulation and radio frequency–microwave double-resonance (RFMDR) spectra were obtained with a Hewlett-Packard 8460A microwave spectrometer as described previously.[13,14] Spectra of two ^{13}C isotopic species were observed in their natural isotopic abundance and the C_3D and C_1D species were observed with samples enriched in deuterium to the extent of 10% and 50%, respectively. Most spectra were obtained at dry ice temperature with sample pressures of 10–20 mtorr.

Quantum Mechanical Methods. Ab initio calculations were performed with Pople's GAUSSIAN 82 series of programs[17] which employed the 6-31G* basis set.[18] Geometry optimizations were performed by employing analytically evaluated atomic forces in a Berny multiparameter search routine.[17] Full basis sets were used and geometries were optimized completely, subject only to molecular symmetry (C_s or C_{2v}) constraints.

Results

Microwave Spectra. Spectral assignments for the isotopic species proceeded in a reasonably straightforward fashion by analogy to the normal isotopic species.[11] Because of the low isotopic abundance (1% and 2%) of the 4-^{13}C and 1-^{13}C isotopic species, respectively, it was possible to observe only the more intense *a*-type R-branch lines. These were assigned unambiguously by means of RFMDR measurements and by careful observations of intensities and their temperature dependence. The much less intense *c*-type ($\mu_c^2/\mu_a^2 = 0.03$) transitions and the weak high-*J* transitions observed for the normal species could not be unambiguously sorted out from the background of excited vibrational-state spectra. The 3-^{13}C spectrum was searched for extensively but could not be extracted from the strong and dense satellite spectra lying near the normal species line.

Table I lists the observed frequencies for the natural abundance spectra. In order to produce *B* and *C* rotational constants with precision comparable to the earlier normal species results, small P^4 centrifugal distortion contributions were subtracted out before fitting the corrected frequencies to the standard rigid rotor model. These corrections have been obtained from the corresponding contributions for the normal species[11] by scaling according to the transition frequencies.[19,20] Thus, in the symbolism of Table I, we obtain hypothetical rigid rotor frequencies from obsd ν–C.D. The precision of the resulting rigid rotor rotational constants in Table II is several times higher than if no distortion corrections were made, although the constants are not greatly different. Note

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Table III. Microwave Spectrum of 1-D Isotopic Species[a]

transition	obsd	obsd − calcd	transition	obsd	obsd − calcd
$2_{11} \leftarrow 1_{01}$	28 300.73	0.06	$12_{2,11} \leftarrow 12_{1,11}$	37 584.52	0.01
$4_{14} \leftarrow 3_{13}$	26 617.17	0.02	$13_{2,12} \leftarrow 13_{1,12}$	36 585.65	0.02
$4_{04} \leftarrow 3_{03}$	26 930.06	−0.01	$14_{2,13} \leftarrow 14_{1,13}$	35 521.08	0.02
$4_{23} \leftarrow 3_{22}$	26 942.83	0.20	$15_{2,14} \leftarrow 15_{1,14}$	34 394.05	0.02
$4_{22} \leftarrow 3_{21}$	26 955.94	−0.15	$16_{2,15} \leftarrow 16_{1,15}$	33 208.29	0.00
$4_{13} \leftarrow 3_{12}$	27 264.58	−0.03	$17_{2,16} \leftarrow 17_{1,16}$	31 968.03	−0.06
$5_{15} \leftarrow 4_{14}$	33 268.71	0.01	$18_{2,17} \leftarrow 18_{1,17}$	30 678.30	−0.02
$5_{05} \leftarrow 4_{05}$	33 652.22	−0.05	$19_{2,18} \leftarrow 19_{1,18}$	29 344.45	0.00
$5_{24} \leftarrow 4_{23}$	33 676.48	0.11	$20_{2,19} \leftarrow 20_{1,19}$	27 972.64	0.02
$5_{23} \leftarrow 4_{22}$	33 703.20	−0.07	$32_{8,25} \leftarrow 31_{9,23}$	32 087.35	−0.01
$5_{14} \leftarrow 4_{13}$	34 077.96	−0.01	$27_{8,20} \leftarrow 28_{7,22}$	29 901.30	0.01
$3_{12} \leftarrow 2_{02}$	35 279.83	−0.05	$35_{10,26} \leftarrow 36_{9,28}$	34 274.44	0.01
$7_{07} \leftarrow 6_{15}$	30 715.26	−0.03	$30_{9,22} \leftarrow 31_{8,24}$	38 837.55	0.00
$8_{08} \leftarrow 7_{16}$	36 789.40	0.02	$39_{11,29} \leftarrow 40_{10,31}$	36 463.04	0.00
$11_{2,10} \leftarrow 11_{1,10}$	38 514.88	−0.03			

[a] All values in MHz. Observed frequencies better than ±0.05.

Table IV. Rotational and Distortion Constants of 1-D Isotopic Species[a]

A	17954.030 ± 0.025[b]
B	3448.918 ± 0.003
C	3287.051 ± 0.007
τ'_{aaaa}	−0.3689 ± 0.0016
τ'_{bbbb}	$-(0.480 \pm 0.033) \times 10^{-2}$
τ'_{cccc}	$-(0.606 \pm 0.053) \times 10^{-2}$
τ'_{bbcc}	$-(0.472 \pm 0.031) \times 10^{-2}$
$\tau'_{aabb} + \tau'_{aacc}$	$-(0.59 \pm 0.39) \times 10^{-2}$

[a] All values in MHz. [b] Uncertainties are the standard deviations.

that the A rotational constants are poorly defined by the R-branch lines.

For the 1-D isotopic species, the 50% enrichment permitted an extensive a- and c-type assignment as for the normal species. These results are presented in Table III, and the constants computed from a Hamiltonian containing terms through P^4[20] are presented in Table IV. On the other hand, the rather low enrichment of the 3-D species, along with its more unfavorable spectral location, permitted observation of only a very few R-branch lines. These measurements are given in Table I. If centrifugal distortion corrections are utilized as previously described, reliable B and C rotational constants are obtained as summarized in Table II.

Microwave Structure. The work reported here, along with the earlier study of the normal species of cyanocyclopropene, has yielded a total of 12 reliable, precise rotational constants. Unfortunately, no isotopic data are available for the nitrogen atom or for C_3. Thus, although substitution (r_s) coordinates[21,22] can be computed for four atoms (by using the plane of symmetry relation $\Delta I_a = \Delta I_b - \Delta I_c$ in three cases), the lack of isotopic data for N and C_3 and the poor precision of the A constant for the 1-^{13}C species prevent the computation of a complete substitution structure. On the other hand, the available 12 precise moments of inertia are sensitive to all of the structural parameters, and by employing the method of Nösberger et al.,[23] we have been able to derive a structure which should be of comparable quality to that of a complete r_s structure.

On following the procedure of Nösberger et al., we obtain a least-squares fit of structural parameters to isotopic *differences* of moments of inertia (I_g (isotope)−I_g (normal), etc.) and to the moments of inertia of the normal species, the differences being weighted 10 times greater than the moments themselves. After elimination of the three poorly determined A rotational constants, this procedure provides 12 least-squares normal equations for the determination of 9 independent molecular structure parameters. Table V presents a summary of the resulting structure with uncertainties estimated by Costain's method.[26,27] In effect, the difference equations lead to "substitution"-type coordinates for all of those atoms which have been isotopically substituted, while the remaining two atoms are located by the moment of inertia equations of the normal species. The least-squares procedure provides the best average fit of the entire data set, and the heavy-atom structure of Table V (with its relatively generous Costain error limits) is expected to approximate the equilibrium structure rather well.

Table V. Experimental Structural Parameters for 3-Cyanocyclopropene and Related Molecules[a]

parameter	3-CNCP[b]	C_3H_4[c]	parameter	CNCP[d]	C_3H_6[e]
C_1C_3	1.511 ± 0.005	1.509	C_1C_2	1.529	1.513
C_1C_2	1.292 ± 0.003	1.296	C_2C_3	1.500	
C_3C_4	1.453 ± 0.006		C_1C_4	1.420	
CN	1.162 ± 0.005		CN	1.161	
C_3H	1.092 ± 0.003	1.088	C_1H	1.087	1.084
C_1H	1.071 ± 0.004	1.072	C_2H	1.083[f]	
$\angle HC_1C_2$	152.3 ± 0.3	149.9	$\angle HCH$	114.6[f]	114.5
$\angle HC_3C_4$	114.2 ± 0.6	114.6[g]	$\angle HC_1C_4$	118.3	
$\angle\beta$[h]	122.9 ± 0.6	122.7	$\angle\beta$[h]	123.4	

[a] Distances in Å, angles in degrees. [b] 3-Cyanocyclopropene, microwave structure; this work. [c] Cyclopropene, microwave structure; ref 24. [d] Cyanocyclopropane microwave structure; ref 8 and footnote 18 of ref 9. [e] Cyclopropane, electron diffraction/spectroscopic structure; ref 25. [f] Assumed. [g] $\angle HC_3H$. [h] Angle between C_4 and C_3 or C_1 and the ring plane.

Table VI. Coordinate Comparisons[a]

atom	coordinate	Table V structure	pure r_s[b]
3-H	a	0.4246	0.4247
	b	0.0	0.0
	c	1.6927	1.6926
1-H	a	1.8143	1.8144
	b	1.5942	1.5947
	c	−0.5331	−0.5304
C_4	a	−1.0326	−1.0322
	b	0.0	0.0
	c	0.118	0.153

[a] Values in Å. [b] Computed by using Kraitchman's equations.

The consistency of the resulting structure can be partially assessed by comparing the atomic coordinates computed from the Table V structure with the r_s coordinates computed from Kraitchman's equations.[2] This comparison is presented in Table VI for both unique hydrogen atoms and for C_4. Note that the 1-C^{13} data cannot be used to compute a reliable set of r_s coordinates for C_1 because of the poor A rotational constant, while

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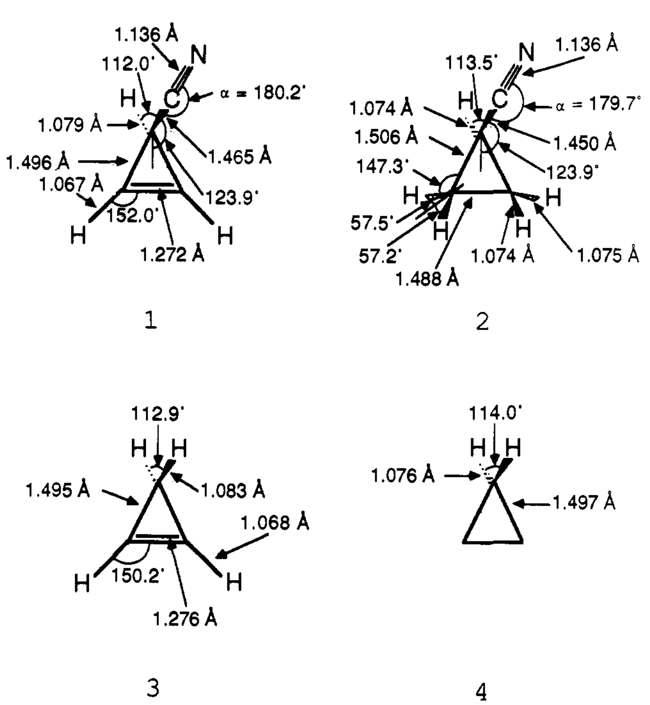


Figure 1. 6-31G* geometry-optimized molecular structures for **1–4**. ($\angle\alpha$ in **1** and **2** lies in the molecular symmetry plane opposite to C_3H and C_1H, respectively.)

Table VII. Changes in Selected Heavy-Atom Structural Parameters for 3-Cyanocyclopropene and Cyanocyclopropane Relative to Related Molecules[a]

parameter	microwave[e]	6-31G*//6-31G*
	3-Cyanocyclopropene	
C_1C_3[b]	+0.002 (7)	+0.001
C_1C_2[b]	−0.004 (4)	−0.004
C_3C_4[c]	+0.033 (9)	+0.015
$\angle\beta$[c]	−0.5 (9)	0.0
	Cyanocyclopropane	
C_1C_2[d]	+0.016 (7)	+0.010
C_2C_3[d]	−0.013 (4)	−0.009

[a] 3-Cyanocyclopropene or cyanocyclopropane bond length or angle minus the corresponding quantity for the reference compound (see Table V and Figure 1); distances in Å, angles in degrees. [b] Relative to cyclopropene. [c] Relative to cyanocyclopropane. [d] Relative to cyclopropane. [e] Estimated maximum uncertainties in last digits are given in parentheses.

the 4-C^{13} and 3-D data are usable since the *A* rotational constants are not required for the in-symmetry-plane atoms. It can be seen that the agreement is generally very good except for the small *c* coordinate of C_4 which is unreliably computed by Costain's method.[21,26]

Ab Initio Geometry-Optimized Calculations. Complete 6-31G*-optimized structures for **1–4** are given in Figure 1. As is generally found, agreement between the experimental and computed structures at this level is variable; much better agreement would be expected if electron correlation were included at the MP2 level or higher. What is important is the agreement between *relative* experimental and geometry-optimized structures on comparing the bond lengths and angles in **1** with the corresponding parameters for closely related molecules such as **2** and **3**. As seen in Table VII, the agreement between theory and experiment is generally very good when structural *differences* are compared. The only parameter for which agreement is not within 0.006 Å is the bond between the ring and substituent (C_3C_4). However, both theory and experiment agree on the key point, viz., that C_3C_4 in **1** is lengthened significantly relative to C_1C_4 in **2**.

Discussion

We have shown in past work that a strong π-acceptor substituent such as cyano produced easily discernible bond length changes (lengthening of C_1C_2 and shortening of C_2C_3) in the cyclopropyl ring,[7-9] which were explainable as arising principally by π-electron donation from the cyclopropane 3e′ HOMO to the cyano π^* LUMO.[28] The question arises then as to whether or not a simple π-conjugation occurs for the 3-cyanocyclopropene case. The cyclopropene $3b_1$ orbital, which is analogous to the cyclopropane 3e′ orbital, occurs at essentially the same energy (within 0.05 eV) as the latter orbital, as determined by both photoelectron spectroscopy[29] and by 6-31G*-optimized ab initio calculations. If the cyclopropene $3b_1 \rightarrow$ cyano π^* donation (Figure 2a) is the dominant interaction, one would expect structural changes in cyanocyclopropene relative to cyclopropene (**3**) comparable to those observed for cyanocyclopropane (**2**) relative to cyclopropane (**4**).

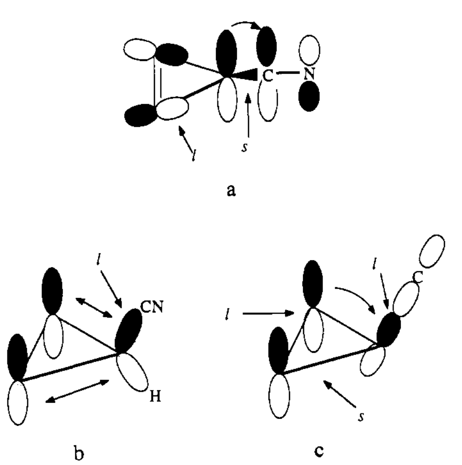
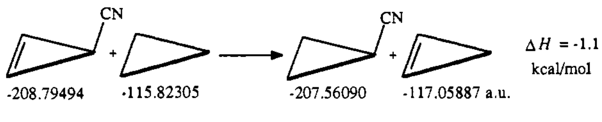


Figure 2. (a) Electron donation from the cyclopropenyl $3b_1$ orbital into the cyano π^* orbital. (b) Electron repulsion between the cyclopropenyl $2b_2$ (π) orbital and the C_3C_4 and C_3H σ orbitals. (c) Electron donation from the cyclopropenyl $2b_2$ (π) orbital into the C_3C_4 σ^* orbital. (Double-headed arrows represent electron repulsion, whereas single-headed arrows represent shifts of electron density. The corresponding structural changes are represented by an s (bond shortening) or an l (bond lengthening).)

From Tables V and VII, we see that although the changes are in the correct directions for the above interaction (C_1C_2 is shortened and C_1C_3 is lengthened relative to cyclopropene), the changes are much smaller than observed in cyanocyclopropane. (Note that the bonds adjacent and opposite to the substituent are C_1C_3 and C_1C_2, respectively, in cyanocyclopropene but C_1C_2 and C_2C_3, respectively, in cyanocyclopropane.) These small relative changes are reflected almost exactly by the relative 6-31G*//6-31G* geometries (Table VII). Clearly some interaction(s) in **1** must differ from the corresponding interaction(s) in **2**.

A further clue as to the nature of an additional effect or effects is provided by the observation that the C_3C_4 bond in **1** is lengthened by 0.033 Å relative to the corresponding bond in **2** (see Table VII). Although the relative 6-31G*-optimized difference is only half as much as the microwave value, the effect is nevertheless large and in the same direction. Thus, the decreased changes in **1** relative to **3** in Table VII discussed above are accompanied by what appears to be reduced conjugation across C_3C_4 in **1** relative to C_1C_4 in **2**. Coupled with this is the fact that a small exothermicity is calculated for isodesmic reaction (1) at the 6-31G*//6-31G* level. This suggests that **1** has a *greater* conjugation energy (or lower repulsion energy) than **2**.



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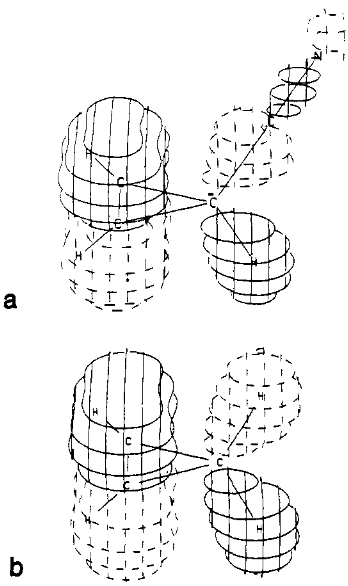

Figure 3. Three-dimensional plots of STO-3G//6-31G* wave functions calculated with the PSI/77 program (ref 30): (a) 3-cyanocylcopropene; (b) cyclopropene.

We propose that (relative to **3**) a reduced cyclopropenyl $2b_2$ (π) $\leftrightarrow$ $\sigma(C_3C_4)$ four-electron repulsion (Figure 2b) coupled with an enhanced cyclopropenyl $2b_2$ (π) $\rightarrow$ $\sigma^*(C_3C_4)$ donation (Figure 2c) make a significant contribution to the ground state of **1**. It can be seen that the second of these effects leads directly to a relative lengthening of C_1C_2 and C_3C_4 and a shortening of C_1C_3 which counterbalances the cyano $3b_1$ $\rightarrow$ cyclopropenyl π^* effects.

This interpretation is supported by the fact that the C_1C_2 π-electron density in **1** is calculated at the 6-31G* level to be 0.014 electron less than that in **3** whereas the total cyano electron density in **1** is 0.007 electron greater than that in **2**. The observation that the CCN unit is calculated to bend slightly away from C_1H in **2** but slightly toward C_3H in **1** is also consistent with this interpretation.

The result of this mixing is illustrated by three-dimensional orbital plots of the HOMOs of **1** and **3**. The wave function at C_3 in **3** (Figure 3b) is moderately large owing to a dominant antibonding mixing of the C_1C_2 π orbital with the CH_2 pseudo-π orbital. In contrast, the corresponding orbital in **1** (Figure 3a) has a smaller contribution from the HC_3CN orbitals. This is consistent with a reduced mixing with $\sigma(HC_3CN)$ and an increased mixing with $\sigma^*(HC_3CN)$ compared to the corresponding orbitals in **3**. Since these mixings offset each other at C_3, the dominant mixing with $\sigma(HC_3H)$ calculated for **3** is attenuated in **1**. This explanation is supported by the fact that the ring π orbital for **1** is calculated to be 1.29 eV lower in energy than that for **3**.

In summary, we conclude that, although the distortion of the three-membered ring in **1** relative to **3** is much less than the corresponding distortion in **2** relative to **4**, there is actually *more* conjugation (and less repulsion) between the cyano group and the ring in **1** than in **2**. Interaction a in Figure 2 is probably present in **1** to an extent comparable to that in **2**, but its structural effect is attenuated by a reduction in interaction b and by an increase in interaction c. This once again illustrates the importance of *both* stabilizing two-electron interactions and repulsive four-electron repulsive interactions in determining the structural effect of substituents in small-ring compounds.

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Registry No. **1**, 38693-83-3; **1**-*1-d*, 107383-60-8; **1**-*3-d*, 107383-61-9; **1**-*1*-^{13}C, 107383-63-1; **1**-*4*-^{13}C, 107383-64-2; **2**, 5500-21-0; 4, 75-19-4; dimethyl phthalate, 131-11-3; dimethyl 3-*anti*-cyano-*exo*-tricyclo-[3.2.2.0^{2,4}]nona-6,8-diene-6,7-dicarboxylate, 6254-43-9; dimethyl 3-*anti*-cyano-*exo*-tricyclo[3.2.2.0^{2,4}]nona-6,8-diene-6,7-dicarboxylate-*3-d*, 107383-62-0; dimethyl 3-*anti*-cyano-*endo*-tricyclo[3.2.2.0^{2,4}]nona-6,8-diene-6,7-dicarboxylate, 6204-44-0.

Velocity Modulation Laser Spectroscopy of Negative Ions: The ν_3 Band of Azide (N_3^-)

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Abstract: Thirty-four transitions in the ν_3 (asymmetric stretch) fundamental of the azide anion have been measured in an NH_3/N_2O discharge by using diode laser velocity modulation spectroscopy. The data, ranging from P(42) to R(62), were fit to a linear molecule effective Hamiltonian through quartic terms. The vibrational band origin was determined to be $\nu_3 = 1986.4672$ (19) cm^{-1} and the rotational constants are $B'' = 0.426\,203$ (57) and $B' = 0.422\,572$ (55) cm^{-1}. Comparisons with ab initio calculations and condensed phase measurements are presented. The observed 2:1 intensity alternation in successive rotational lines establishes the centrosymmetric structure of the anion ($r_0 = 1.188402$ (82) Å).

The azide anion is of considerable importance in both organic and inorganic chemistry. For example, the reaction of the azide ion with carboxylic acids to form acyl azides has provided an essential precursor for the synthesis of amides and amines.[1] In transition-metal complexes, azide functions as a pseudohalide ligand, which can yield bridged as well as unidentate complexes.[2] The detailed chemistry of azides is summarized in the text by Patai.[3]

All previous spectroscopic studies of azide have been carried out in condensed phases. N_3^- was observed in infrared and Raman

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