Preparation of Labeled Diazirine [^{15}N]-24. 3-(Trifluoromethyl)benzonitrile (2.983 g, 0.0172 mol) was dissolved in 17 mL of anhydrous methanol, and 1.0 mL of 1.88 M NaOMe in methanol (0.001 88 mol) was added under nitrogen. The reaction mixture was stoppered and allowed to stir for 48 h at room temperature. ^{15}N-Labeled ammonium chloride (0.9688 g, 0.0183 mol of 99.1% ^{15}N enriched; Isotech, Inc.) was added and the suspension stirred for 35 h at room temperature. The mixture was filtered, and the unreacted ammonium chloride in the filter was washed with a small amount of anhydrous methanol. The combined filtrates were concentrated with a rotary evaporator, and the crystals were slurried with ether. The ether was then decanted. This procedure was carried out a total of five times in order to remove unreacted 3-(trifluoromethyl)benzonitrile. The yield of ^{15}N-labeled 3-(trifluoromethyl)benzamidine hydrochloride was 3.0448 g (79%).

A NaOBr solution was prepared from 6.28 g of NaOH in 80 mL of water by the addition of 6.60 g of bromine. When all the bromine had reacted, 4.28 g of NaBr was added and the flask swirled to dissolve the NaBr. This solution was used immediately in the oxidation of the ^{15}N-labeled 3-(trifluoromethyl)benzamidine hydrochloride. The salt prepared above (3.044 g, 0.0135 mol) was dissolved in 40 mL of freshly distilled dimethyl sulfoxide, and 45 mL of hexanes was added followed by 3.98 g of NaBr. The mixture was placed in an ice–water bath, and before the DMSO could freeze, a small amount of the freshly prepared NaOBr solution was added. The solution was allowed to cool thoroughly, and the remaining NaOBr solution was added in portions over a 5-min period. The mixture was stirred at 0 °C for 70 min, and the organic phase was separated. The aqueous phase was extracted with two additional portions of ether, and the combined organic extracts were washed with two portions of water and with saturated NaCl solution. The organic phase was dried over $MgSO_4$, and the solvents were removed with a rotary evaporator. The residue was chromatographed on 19.6 g of silica gel and eluted with 200 mL of hexanes. The solvent was removed with a rotary evaporator, and the residue (0.456 g) was distilled (safety shield) to give 0.314 g (9%) of diazirine [^{15}N]-**24**, bp <25 °C (0.05 mm).

Reaction of [^{15}N]-24 with Sodium Azide. Sodium azide (0.171 g) was dissolved in 4.6 mL of DMSO. Diazirine [^{15}N]-**24** (0.231 g) was added, and the mixture was stirred at room temperature for 71 h. Ether was then added, and the mixture was extracted with two portions of water and with saturated NaCl solution. The ether solution was dried over $MgSO_4$. Solvent removal with a rotary evaporator left 0.151 g (81%) of *m*-(trifluoromethyl)benzonitrile, which was identical by ^{1}H NMR and gas chromatographic retention time with an authentic sample of *m*-(trifluoromethyl)benzonitrile. The ^{15}N NMR and ^{13}C NMR spectra are shown in Figures 4 and 5. Under the same spectral conditions, unlabeled *m*-(trifluoromethyl)benzonitrile showed no ^{15}N signal. The mass spectrum of the product shows peaks at *m/e* 171 (100%) and 172 (60.14%). Unlabeled *m*-(trifluoromethyl)benzonitrile showed peaks at *m/e* 170 (30.34%), 171 (100%), and 172 (8.96%). The ratio of [^{14}N]-**25** to [^{15}N]-**25** was calculated from the 171/172 ratio by assuming that the *m/e* 171 peak is due to unlabeled [^{14}N]-**25** and the m − 1 peak (30.34%) of labeled [^{15}N]-**25**. The peak at *m/e* 172 is due to [^{15}N]-**25** and the m + 1 peak (8.96%) of [^{14}N]-**25**.

Note Added in Proof. Since the acceptance of this manuscript, we have learned that Professor W. P. Dailey has independently carried out a study of the reaction of [^{15}N]-**1** with azide ion. We thank Professor Dailey for providing us with a preprint of his manuscript which will be published in *Tetrahedron Lett.*

Acknowledgment is made to the National Science Foundation for financial support of this research.

Registry No. 1, 4222-25-7; **1**-^{15}N, 123811-64-3; **1**-$^{15}N_2$, 123811-65-4; 7, 100-47-0; 7-^{15}N, 24949-34-6; **11**, 123811-70-1; **16**-^{15}N, 123811-66-5; **16**-$^{15}N_2$, 123811-67-6; **22**, 95911-62-9; **23**, 95911-61-8; **24**-^{15}N, 123811-68-7; **25**, 368-77-4; **25**-^{15}N, 123811-69-8; [N=N=^{15}N]$^-$, 33095-00-0; Bu_4NN_3, 993-22-6; CH_3-*p*-C_6H_4CN, 104-85-8; CH_3O-*p*-C_6H_4CN, 874-90-8; $^{15}NH_4Cl$, 39466-62-1; NaOBr, 13824-96-9.

A Single Crystal Molecular Structure Determination and Theoretical Calculations on Alkynyl Carboxylate Esters[†]

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Abstract: A single crystal molecular structure is reported for propynyl *p*-nitrobenzoate, a member of the new class of alkynyl esters. An experimentally determined C_{sp}–O bond length of 1.366 (9) Å is observed for the first time. The C≡C bond length is 1.155 (9) Å. The structural features of the ester moiety in the alkynyl ester are compared to the analogous saturated and unsaturated (vinyl, aryl) esters. Ab initio molecular orbital calculations are reported for hydroxyacetylene, ethynyl formate (**7**), propynyl formate, ethynyl acetate, vinyl formate (**10**), and methyl formate (**11**). at the 6-31G* level the most stable conformation of **7** is Z (or syn) and the calculated C≡C—O and C≡C bonds are 1.312 Å and 1.179 Å, respectively. By use of model compounds, it is estimated that the addition of correlation energy would increase these bond distances by 0.01–0.02 Å. Possible reasons for the experimental/theoretical discrepancies are discussed, and it is concluded that the theoretical values are probably closer to reality. In agreement with this conclusion, good agreement is observed between the experimental and theoretical geometries, for vinyl formate (**10**). At the 6-31G* level the calculated energies of hydrolyses for **7**, **10**, and **11** are computed to be −8.9, −4.3, and +1.5 kcal/mole, respectively. The calculated electronic structures, charge distributions, and dipole moments for acetylenic esters are also discussed.

Esters, as well as acetylenes, are ubiquitous, important, and valuable organic functionalities with a great variety of uses in mechanistic, synthetic, and bioorganic chemistry. Recently, we reported the preparation and characterization of alkynyl sulfonates,[1] **1**, alkynyl carboxylates,[2] **2**, and alkynyl phosphates,[3] **3**, which are members of the family of hitherto unknown, novel

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[†] Dedicated to Professor Paul v. R. Schleyer on the occasion of his 60th birthday.

[‡] University of Utah.

[§] Techion, Israel Institute of Technology.

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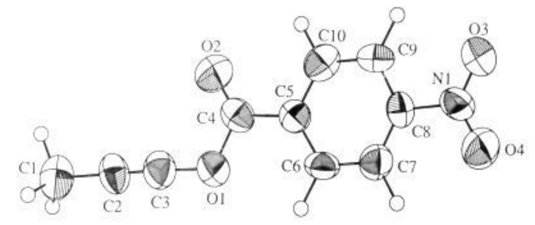


Figure 1. ORTEP[31] of propynyl *p*-nitrobenzoate (**4**).

Table I. Summary of Crystallographic Data

molecular formula	O4, N, C10, H7
molecular weight	205.17
crystal system	monoclinic
space group	*P*2(1)/*c*
a	7.225 (2)
b	19.612 (6)
c	13.775 (4)
β	100.92 (2)
V	1916.53 Å^3
Z	8
d(calc), g/cm^3	1.422
T	15.0 °C
crystal dimensions, mm	0.41 × 0.36 × 0.30 mm along direct crystal axes
diffractometer	Syntex P$\bar{1}$
radiation	K_α–Mo (0.71073) Å
data collection method	Θ–2Θ
scan speed	variable (3.0–8.0) deg/min
reflections measured	3216:h(0,8), k(0,22), 1(−15,15)
scan range	1.0° below $K\alpha_1$ to 1.0° above $K\alpha_2$
2θ limits	3.0–48.0°
total bkdg. time/scan time	0.5
no. of reflections between std.	98
total unique data	2688
observed data, $I > 2.6\sigma(I)$	1455
no. absorption correction was applied	1.049
no. of variables	271
R (averaging)	0.029, 0.023
max. shift/error	0.0
$R(F)$	0.0583
$R_w(F)$	0.0589
goodness of fit	1.51
max. diff. Fourier peak	0.189 e/Å^3

acetylenic esters that combine two of the common, simple, and most interesting organic functionalities into a single, unique derivative.

$$\underset{\mathbf{1}}{RC{\equiv}COSO_2Ar} \qquad \underset{\mathbf{2}}{RC{\equiv}COC(O)R'}$$

$$\underset{\mathbf{3}}{RC{\equiv}COP(O)(OR')_2}$$

Fundamental, intrinsic properties such as molecular structure, bonding, dipole moments, electron distributions, etc. of all classes of molecules, and new ones in particular, are of inherent interest as they govern the nature, behavior, and reactivity of the species involved. Specifically, there is considerable current interest and research activity in systematic molecular structure analysis and bonding and its relationship between chemical dynamics and reactivity.[4,5] Hence, we report on some of these properties for alkynyl carboxylates, members of the above new class of acetylenic esters. Both experimental measurements and theoretical calculations and comparisons are reported.

Results and Discussion

The great majority of common, simple esters of all types, such as sulfonate, carboxylate, and phosphate, are liquids at standard conditions. The new acetylenic esters **1**–**3** are no exception with only a very few solids at ordinary conditions among the dozens of compounds prepared to date.[1-3] Of these, to date, only propynyl *p*-nitrobenzoate (**4**) gave single crystals suitable for X-ray structure determination. Of the sulfonate esters,[1] only propynyl *p*-nitrobenzenesulfonate (**5**) is a low-melting solid, but until now we have been unable to obtain suitable single crystals for structure determination. No solid alkynyl phosphate esters[3] have been observed to date.

Table II. Bond Distances for Ester **4** in Angstroms[a]

atom 1	atom 2	distance	distance
O1	C3	1.361 (9)	1.371 (9)
O1	C4	1.363 (8)	1.336 (9)
O2	C4	1.186 (8)	1.216 (8)
O3	N1	1.206 (7)	1.215 (7)
O4	N1	1.216 (8)	1.199 (7)
N1	C8	1.495 (9)	1.478 (9)
C1	C2	1.45 (1)	1.43 (1)
C2	C3	1.151 (9)	1.16 (1)
C4	C5	1.48 (1)	1.48 (1)
C5	C6	1.38 (1)	1.401 (9)
C5	C10	1.396 (9)	1.378 (9)
C6	C7	1.40 (1)	1.35 (1)
C7	C8	1.349 (9)	1.367 (9)
C8	C9	1.385 (9)	1.399 (9)
C9	C10	1.39 (1)	1.374 (9)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table III. Bond Angles for Ester **4** in Degrees[a]

atom 1	atom 2	atom 3	angle	angle
C3	O1	C4	113.7 (6)	116.2 (7)
O3	N1	O4	124.1 (8)	123.7 (7)
O3	N1	C8	118.8 (7)	118.2 (7)
O4	N1	C8	117.0 (7)	118.1 (7)
C1	C2	C3	177.9 (9)	179.0 (1)
O1	C3	C2	177.0 (1)	179.0 (1)
O1	C4	O2	122.9 (8)	123.5 (9)
O1	C4	C5	111.3 (7)	111.8 (8)
O2	C4	C5	125.6 (8)	124.8 (9)
C4	C5	C6	124.6 (8)	116.5 (7)
C4	C5	C10	116.1 (7)	124.0 (8)
C6	C5	C10	119.3 (7)	119.5 (7)
C5	C6	C7	120.3 (7)	120.1 (7)
C6	C7	C8	118.1 (7)	119.5 (7)
N1	C8	C7	119.8 (7)	119.6 (7)
N1	C8	C9	115.4 (7)	118.1 (6)
C7	C8	C9	124.8 (7)	122.3 (8)
C8	C9	C10	115.9 (7)	117.2 (7)
C5	C10	C9	121.7 (7)	121.3 (7)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

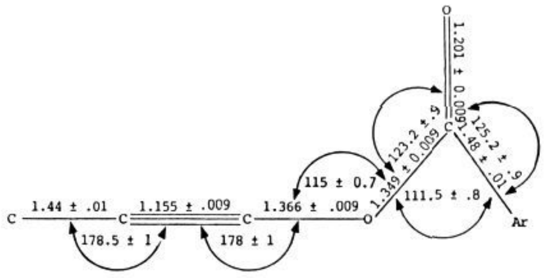
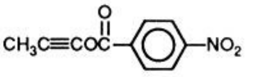


Figure 2. Summary of key structural features (and their esd) of propynyl *p*-nitrobenzoate (**4**). Torsional angles between C_3–O_1–C_4–O_2 and C_3–O_1–C_4–C_5 are 0.80° and 178.2°, respectively (for numbering, see Figure 1).



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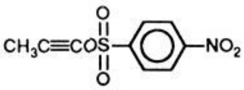

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X-ray Structure of Propynyl *p*-Nitrobenzoate (4). A suitable single crystal of **4** was subjected to standard X-ray analysis. The relevant crystal and structural data are summarized in Tables

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Table IV. Positional Parameters and Their Estimated Standard Deviations[a]

atom	*x*	*y*	*z*	*B*, Å^2
O1	0.9627 (7)	−0.4514 (3)	0.8643 (4)	6.1 (1)
O1′	0.5074 (7)	0.1458 (3)	0.8309 (4)	6.7 (2)
O2′	0.7416 (9)	0.2207 (3)	0.8812 (5)	8.3 (2)
O2	1.2049 (8)	−0.5242 (3)	0.9009 (4)	7.0 (2)
O3′	1.1373 (8)	−0.1174 (3)	0.8798 (4)	7.2 (2)
O3	1.8151 (8)	−0.2525 (3)	0.9491 (4)	7.3 (2)
O4′	1.3646 (8)	−0.0474 (3)	0.9173 (4)	7.4 (2)
O4	1.5843 (9)	−0.1823 (3)	0.9228 (5)	9.1 (2)
N1′	1.1998 (8)	−0.0600 (3)	0.8940 (4)	5.3 (2)
N1	1.6489 (9)	−0.2398 (3)	0.9304 (5)	5.9 (2)
C1	0.614 (1)	−0.6087 (4)	0.8190 (6)	6.8 (2)
C1′	0.136 (1)	0.2967 (4)	0.7985 (7)	7.4 (3)
C2′	0.271 (1)	0.2425 (4)	0.8103 (6)	6.1 (2)
C2	0.743 (1)	−0.5517 (4)	0.8381 (6)	5.6 (2)
C3	0.847 (1)	−0.5068 (4)	0.8506 (6)	5.9 (2)
C3′	0.380 (1)	0.1984 (4)	0.8206 (6)	6.2 (2)
C4	1.149 (1)	−0.4673 (4)	0.8915 (5)	4.9 (2)
C4′	0.688 (1)	0.1625 (4)	0.8626 (6)	6.0 (2)
C5′	0.813 (1)	0.1023 (4)	0.8693 (5)	4.4 (2)
C5	1.268 (1)	−0.4051 (4)	0.9009 (5)	4.6 (2)
C6′	1.006 (1)	0.1142 (4)	0.9012 (6)	5.6 (2)
C6	1.200 (1)	−0.3394 (4)	0.8917 (5)	4.9 (2)
C7	1.325 (1)	−0.2841 (4)	0.9010 (6)	5.6 (2)
C7′	1.130 (1)	0.0620 (4)	0.9074 (6)	5.4 (2)
C8′	1.065 (1)	−0.0026 (4)	0.8849 (5)	4.4 (2)
C8	1.511 (1)	−0.2974 (4)	0.9205 (5)	4.6 (2)
C9′	0.873 (1)	−0.0170 (4)	0.8529 (5)	5.1 (2)
C9	1.590 (1)	−0.3620 (4)	0.9313 (5)	5.0 (2)
C10	1.463 (1)	−0.4159 (4)	0.9211 (6)	5.6 (2)
C10′	0.750 (1)	0.0368 (4)	0.8466 (5)	4.9 (2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

I–IV, and the ORTEP structure is shown in Figure 1. The unit cell of the only suitable sample contained two crystallographically independent molecules in the asymmetric unit. This provides two *independent* measurements of each structural parameter. Bond lengths and angles would not be expected to be affected by the slightly different environments in which the two molecules are found. Torsion angles are likely to be more sensitive to the molecular environment, but also in this case rather small changes are expected. It is therefore reasonable to use the *average* values of the two independent measurements of the geometrical parameters of **4** as the best available experimental values. The esd's of these average values were calculated by multiplying each of the independent esd values by a factor of 1.4[6] and by taking their mean (i.e., $\sigma_{\text{mean}} = \sqrt{1/\sum(1/\sigma_i^2)}$). These esd values are probably underestimated, as for some parameters the spread of the independent measured values is significantly larger than the calculated esd values (e.g., the O—C(=O) bond length). Figure 2 displays the average values (and the corresponding esd) of the key structural features of **4**. For comparison, recently reported values of Dunitz[7] for the key structural characteristics of alkyl and aryl carboxylic esters are summarized in Figure 3.

The data reveal a number of interesting structural features of this novel alkynyl benzoate ester. Specifically, the molecule, as expected, is essentially a linear acetylene. Likewise, like all known acyclic esters,[7] the molecule adopts the *Z*, or antiperiplanar (syn), conformation around the O—C(=O) bond. The carbon–carbon triple bond (see also below) and the other carbon–carbon bonds and angles are all within commonly accepted standard values.[8]

Particularly interesting are the structural features of the ester moiety of **4** and their comparison to saturated, vinylic, and aromatic esters.

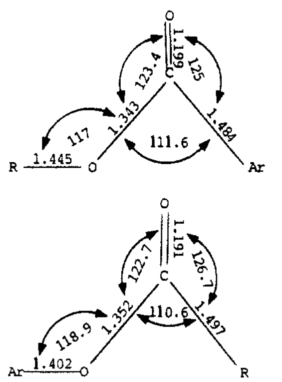

Figure 3. Summary of typical key structural characteristics of alkyl–aryl and aryl–alkyl carboxylic esters.[7,14]

Table V. Total Energies (in Hartrees) of the Most Stable Conformations of Compounds **7–12**[a,b]

	theoretical method		
compd	6-31G*	MP2/6-31G*	MP3/6-31G*
7S[c,d]	−264.39893	−265.11434	−265.11792
7A[e]	−264.39623	−265.11144	−265.11516
10	−265.63351	−266.35606	
11	−227.78942	−228.39296	−228.40399
12[f]	−151.66164	−152.08222	−152.09104

[a] All structures were optimized at 6-31G*. [b] The total energies at 3-21G of the fully optimized **8** and **9** are −301.76062 and −301.75474 hartrees, respectively. [c] The total energy is −262.92537 hartrees at 3-21G//3-21G. [d] Dipole moment (6-31G*) = 1.53 D. [e] Dipole moment (6-31G*) = 3.22 D. [f] The total energies are −152.09815 and −152.09291 hartrees at MP2/6-31G*//MP2/6-31G* and MP3/6-31G*//MP3/6-31G*, respectively.

In recent, elegant studies, Kirby and co-workers[9–11] have shown that there are considerable variations of bond lengths and bond angles, often systematic, even within the same class of molecules as a function of substitution. They pointed out that bond length variations in particular are highly sensitive to the electronic effects of substituents and suggest that they often correlate with reactivity.[9–11] However, the latter conclusion was recently questioned.[12] In spite of the variation of specific bond length with a particular substitution pattern noted by Kirby,[9–11] the bond lengths of the ester moiety of **4** are, with one notable exception, remarkably close to those of saturated alkyl–aryl and aryl–alkyl esters as seen in Figures 2 and 3. The exception, and particularly noteworthy, is the $C\equiv C{-}O$ acetylenic—oxygen bond length of 1.366 (9) Å. To our knowledge this is the first experimentally determined and reported bond length for a C_{sp}–O single bond.[13] It is significantly shorter than either the C(sp^3)–O bond of saturated esters or the C(sp^2)–O bonds of unsaturated[14,15] or aryl esters,[7] as is evident from the comparison of Figures 2 and

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(7) Schweizer, W. B.; Dunitz, J. D. *Helv. Chim. Acta* **1982**, *65*, 1547.

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(11) For a recent series of 13 papers by Kirby's group: Jones, P. G.; Edwards, M. R.; Kirby, A. J. *Acta Crystallogr.* **1989**, *C45*, 252 and preceding papers in the same issue.

(12) Burgi, H.-B.; Dubler–Steudle, C. D. *J. Am. Chem. Soc.* **1988**, *110*, 7291.

(13) The C_{sp}–O *double bond* length in CO_2 is 1.162 Å; see: Courtoy, C.-P. *Ann. Soc. Sci. Bruxelles, Ser. 1* **1959**, *73*, 5.

(14) Only a very limited number of experimental $C{=}C{-}O$ bond lengths for vinyl (enol) esters are known. Thus in vinyl formate (**10**), the C—O bond distance is 1.397 Å.[15a] In the highly congested $Mes_2C{=}CMes(OCOCH_3)$ it is 1.39 Å[15b] and in $(CH_3CO_2)(CN)C{=}C(OCOC_6H_4NO_2\text{-}p)(C_6H_4NO_2\text{-}p)$ it is 1.382 Å.[15c] These values are practically the same as the average aryl–O bond of aryl esters in Figure 3 used to model the C–O bond length.

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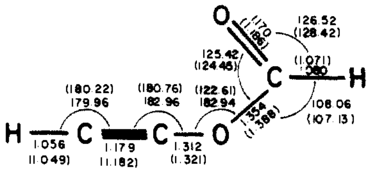
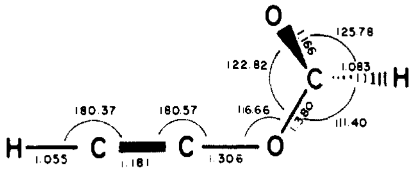
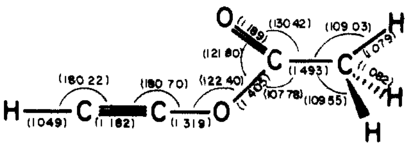


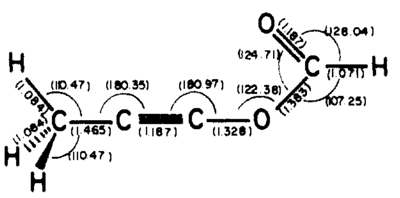
7S



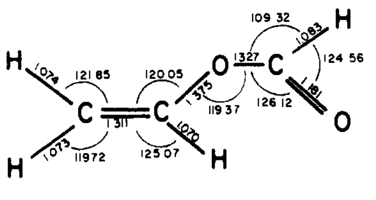
7P



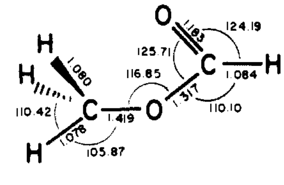
8S



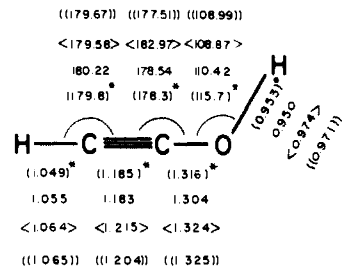
9S



10



11



12

Figure 4. Optimized geometries of the most stable conformations of compounds **7**, **10**, **11**, and **12**. The following symbols were used to indicate optimized geometrical parameters at various levels of theory: 6-31G*, no brackets; 3-21G, round brackets; 4-31G, round brackets with an additional asterisk; MP2/6-31G*, broken brackets; MP3/6-31G*, double round brackets.

3. It is interesting to compare this trend in C–O bond length in going from alkane to alkyne substitution with the analogous trend[4] in C–C bond length as discussed below in conjunction with the results of the theoretical calculations.

Theoretical Calculations. In order to gain further insight into the nature of the chemical bonding in alkynyl carboxylate esters, we have carried out a series of molecular orbital calculations. These include calculations for three simple alkynyl esters **7**–**9** and for three model compounds, ethenyl formate (**10**), methyl formate (**11**), and hydroxyacetylene (**12**). In general several conformations were considered for each ester.

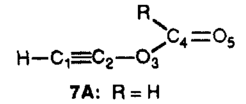
$HC(O)OC{\equiv}CH$ **7** $CH_3C(O)OC{\equiv}CH$ **8**

$HC(O)OC{\equiv}CCH_3$ **9** $HC(O)OCH{=}CH_2$ **10**

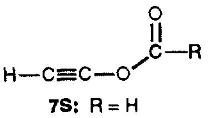
$HC(O)OCH_3$ **11** $HC{\equiv}COH$ **12**

Calculations used standard molecular orbital theory and were carried out with the GAUSSIAN 82 series of programs,[16] using gradient minimization techniques for geometry optimizations.[17] In most cases the molecular geometries were optimized with both the split-valence 3-21G basis set[18a] and the polarized 6-31G* basis set.[18b] To obtain more reliable energies the effect of electron correlation energy was evaluated by using the Møller–Plesset perturbation theory,[19] up to second or third order (a single-point MP3/6-31G* calculation at the optimized 6-31G* geometry is denoted as MP3/6-31G*//6-31G*). The total energies of all the molecules that were calculated are given in Table V, and the optimized geometries of the most stable conformers are presented in Figure 4.

a. Geometries and Conformations. The simplest acetylenic ester, ethynyl formate (**7**), exists in two rotamers, **7A** and **7S**, both having essentially a linear C≡C—O unit. In **7A** the $C_2O_3C_4O_5$ dihedral angle is 180° (i.e., A = anti) and in **7S** this angle is 0° (i.e., S = syn). **7A** and **7S** are *E* and *Z* rotamers with respect to the ester O_3–C_4 bond. The syn conformation, **7S**, is calculated to be more stable than **7A** by 1.7 kcal mol^{-1} (MP3-G-31G*//6-31G* and 6-31G*//6-31G*, 2.2 kcal mol^{-1} at 3-21G//3-21G). It is interesting that the **7S**–**7A** energy difference is not sensitive to the addition of correlation energy in contrast to the energy differences between the analogous rotamers of formic and acetic acid and of methyl formate and acetate.[20a] The *E*–*Z* energy difference in **7** is significantly smaller than in methyl formate (6.0 kcal mol^{-1} at MP3/6-31G**//6-31G*).[20a] The syn conformer is also the



7A: R = H
8A: R = CH_3



7S: R = H
8S: R = CH_3

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(16) Binkley, J. S.; Whitesides, R. A.; Raghavachari, K.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Frisch, M. J.; Kahn, L. R.; Pople, J. A. *GAUSSIAN 82 Release A*; Carnegie-Mellon University: Pittsburgh, PA, 1982.

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(18) (a) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939. Gordon, M. S.; Binkley, J. S.; Pople, J. A.; Pietro, W. J.; Hehre, W. J. *Ibid.* **1982**, *104*, 2797. (b) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213. Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654.

(19) (a) Miller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 1618. (b) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem., Symp.* **1976**, *10*, 1.

(20) (a) Calculations: Wiberg, K. B.; Laidig, K. E. *J. Am. Chem. Soc.* **1987**, *109*, 5935. (b) Experimental: Harmony, M. D.; Laurie, V. W.; Kuczkowski, R. L.; Schwendeman, R. H.; Ramsay, D. A.; Lovas, F. L.; Lafferty, W. J.; Maki, A. G. *J. Phys. Chem. Ref. Data* **1979**, *8*, 619. (c) MO calculations: Wiberg, K. B.; Martin, E. *J. Am. Chem. Soc.* **1985**, *107*, 5035. (d) Experimental: Hilderbrandt, R. L.; Andreassen, A. L.; Bauer, S. H. *J. Phys. Chem.* **1970**, *74*, 1586. (e) Experimental: Iijima, T.; Kimura, M. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 2159.

most stable rotamer of ethynyl acetate (**8**). Conformer **8A** is by 3.8 kcal mol^{-1} (3-21G) higher in energy than **8S**. This 3-21G energy difference is probably too large (as shown by the higher level calculations for **7**). However, it is expected that also at higher levels of theory the *E*–*Z* energy difference in **8** will remain by ca. 1–2 kcal mol^{-1} higher than in **7**. This is reasonable because the methyl group is expected to exert a larger steric effect in the *E* (or A) rotamer than in the *Z* (or S) rotamer. One of the methyl hydrogens in **8S** eclipses the carbonyl group (Figure 4) as was found also for other carbonyl compounds such as acetic acid,[20a,b] acetone,[20c,d] and acetaldehyde.[20c,e] The X-ray structure of propynyl *p*-nitrobenzoate (**4**) shows that this acetylenic ester also adopts the syn(*Z*) conformation around the ester bonds. The calculations provide additional insight into this preference, showing that it is not due to crystal forces or to the presence of the bulky *p*-nitrophenyl substituent which disfavors the more sterically congested anti conformation. Rather, the syn rotamer is inherently preferred over the anti rotamer so that this conformation is predicted to predominate even when the substituent R which is attached to the acyl carbon is small, as in esters **7**–**9**. We note that in adopting the syn conformation the alkynyl esters are similar to all other known acyclic esters which uniformally adopt the syn (or *Z*) conformation.[7]

Comparison of the calculated bond lengths and bond angles of **7**–**9** (Figure 4) with the experimental data of **4** (Figure 2) reveals an overall reasonable agreement, considering the fact that the effect of the *p*-nitrobenzoyl substituent is unknown. However, a difference between theory and experiment is revealed in the most interesting region of the molecule, i.e., around the C≡C—O unit. In **7S**, the calculated C(sp)–O bond distance is 1.312 Å at 6-31G* and 1.321 Å at 3-21G. In **4**, the experimentally determined C(sp)–O distance is significantly longer, 1.366 ± 0.009 Å. The experimental–theoretical difference of 0.054 Å is considerably larger than is usually found at this level of theory.[21] A smaller, although still substantial, experimental–theoretical difference is also found in the acetylenic C≡C bond length which in **7S** is calculated to be 1.179 Å (6-31G*, 1.182 Å at 3-21G) compared with the experimentally determined C≡C distance in **4** of 1.155 ± 0.009 Å.

The discrepancy between the calculated geometry of **7** and the observed geometry of **4** may be due to several factors: (a) the effect of the methyl and the *p*-nitrophenyl substituents, (b) an inadequate basis set, (c) the neglect of electron correlation, (d) experimental errors, or to some combination of a–d. We attempted to evaluate which of these effects is the major contributor to the relatively large experimental–theoretical differences in the C≡C—O and C≡C bond lengths.

To examine the effect of substitution on the geometry, we have carried out calculations for **8** and **9**. Methyl substitution either at the acetylenic terminus or at the carbonyl slightly elongates *both* bonds. The C≡C and C(sp)—O bonds in **9** are elongated by 0.005 and 0.007 Å, respectively, compared with **7**. In **8** the effect of the methyl is even smaller. AM1 calculations[22] for **4** show that the effect of the *p*-nitrophenyl substituent on the geometry is also very small. The calculated AM1 C≡C and C≡C—O bond lengths in **4** are 1.194 and 1.332 Å, respectively, compared with 1.192 and 1.332 Å, respectively, in **7S**. The conclusion is that the substituents present in **4** cannot be responsible for the experimental–theoretical discrepancy.

Another possible explanation for the discrepancy is that the level of theory that we use for geometry optimizations is not adequate. For example, it is well known that single determinant Hartree–Fock theory usually produces bond lengths which are too short.[21] To evaluate the effect of correlation energy on the calculated geometries of acetylenic esters, we have carried out 6-31G*, MP2/6-31G*, and MP3/6-31G* geometry optimizations for acetylenic alcohol **12** (unfortunately, **7** is too large for such calculations).[23] These calculations give the following bond lengths (Figure 4): 1.183 Å (6-31G*) and 1.204 Å (MP3/6-31G*) for the C≡C bond and 1.304 Å (6-31G*) and 1.325 Å (MP3/6-31G*) for the C≡C—O bond. Note that the C≡C bond length is acetylene is calculated to be 1.185 Å at 6-31G*, 1.218 Å at MP2/6-31G*, and 1.206 Å at MP3/6-31G*. The experimental C≡C bond distance of 1.203 Å is in good agreement with the MP3/6-31G* prediction.[21] Based on the experience with **12**, it is reasonable to assume that the addition of electron correlation in **7** will lengthen the C≡C and C≡C—O bonds by 0.01–0.02 Å, thus reducing the experimental–theoretical difference for the ester C≡C—O bond but at the same time increasing this gap for the acetylenic bond. Thus, electron correlation alone cannot be responsible for the above-mentioned unusually large bond-length discrepancies between theory and experiment.

Another possibility is that the experimental–theoretical differences are due to the fact that while the experimental data for **4** were taken at room temperature, the calculations refer to the molecule in its vibrational state at 0 K.[21] Thus, interatomic distances from X-ray data obtained at room temperature tend to be too short by ca. 0.01–0.02 Å because of the effects of rigid-body and internal molecular vibrations in the crystal.[7] However, this effect alone also cannot account for the discrepancy because it should apply to both the C≡C and the C≡C—O distances. Thus, if we apply a lengthening correction of 0.01–0.02 Å for this effect and for the correlation energy effect, then the experimental–theoretical agreement for the C≡C—O bond will be good (e.g., within 0.02 Å), but the theoretical C≡C bond distance will be much too long (i.e., by 0.06–0.07 Å). On the basis of the above analysis, we conclude that the experimental–theoretical discrepancy is due to a large extent to inaccuracies in the experimental determinations. Furthermore, the fact that for some parameters (e.g., the O_3–C_4 bond length) the two independent structural determinations differ significantly points to substantial experimental uncertainties in the relevant geometrical parameters. We also note that for the *sum* of the C≡C and the C≡C—O distances the theoretical and experimental values (theoretical = 2.491 Å, experimental = 2.521 ± 0.013 Å) are in a better agreement (i.e., within ca. 2 esd units of each other) than for each of these distances separately. Thus, if in fact the C≡C bond is longer than was actually determined (e.g., by 0.03 Å), this will bring the experimental and theoretical C≡C—O distances into a much closer agreement. Support for this possibility may be found in the fact that the experimentally determined C≡C bond distance in **4** of 1.155 Å is significantly shorter than found in other acetylenes, and it is in fact one of the shortest acetylenic bonds known.[24] Thus, in the 350 acetylenes for which structures were determined, the average C≡C bond length is 1.181–1.183 Å and only a few structures have C≡C distances shorter than 1.167 Å.[24] On the other hand, we note that the X-ray data of **4** does not reveal a particularly large thermal motion along the C≡C—O axis, which would be expected according to the above suggestion.

At this point the discrepancy between theory and experiment regarding the distances within the C≡C—O unit is not fully understood and we hope to clarify this in the future as more experimental data become available. However, we think that it is due to a large extent to inaccuracies in the experimental structure caused by the two crystallographically independent molecules in the unit cell. The good agreement between experimental and theory for the geometry of the closely related vinylic ester **10** (see below) supports this conclusion. Finally, we also note that in **7**–**9** the angles between the carbonyl group and the atom attached to it (e.g., the HCO angle in **7**) are much smaller than 120°, as noted by Wiberg to be the case around other carbonyl groups.[20a]

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[21] Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley-Interscience: New York, 1986.

[22] Dewar, M. J. S.; Zoelisch, E. F.; Healy, J. J. P.; Stewart, *J. Am. Chem. Soc.* **1985**, *107*, 3902. QCPE Program No. 506.

[23] Ethynol **12** was recently generated in an argon matrix: Hochstrasser, R.; Wirz, J. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 181. For a previous gas-phase detection: van Baar, B.; Wieske, T.; Terlouw, J. K.; Schwarz, H. *Ibid.* **1986**, *25*, 282. For PhC≡COH in solution, see: Chiang, Y.; Kresge, A. J.; Hochstrasser, R.; Wirz, J. *J. Am. Chem. Soc.* **1989**, *111*, 2355.

[24] Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1–S19.

Chart I. Comparison of Experimental (A, Top) and Calculated (6-31G*; B, Bottom) C–O and C–C Bond Lengths as a Function of C-Hybridization for Esters and Hydrocarbons

A

$$\text{C–C}\overset{1.445\ \text{Å}}{\text{———}}\text{O} \quad \Delta = 0.043\ \text{Å} \quad \text{C=C}\overset{1.402\ \text{Å}}{\text{———}}\text{O} \quad \Delta = 0.036\ \text{Å} \quad \text{C}\equiv\text{C}\overset{1.366\ \text{Å}}{\text{———}}\text{O}$$

$$\text{C–C}\overset{1.538\ \text{Å}}{\text{———}}\text{C}< \quad \Delta = 0.031\ \text{Å} \quad \text{C=C}\overset{1.507\ \text{Å}}{\text{———}}\text{C}< \quad \Delta = 0.043\ \text{Å} \quad \text{C}\equiv\text{C}\overset{1.464\ \text{Å}}{\text{———}}\text{C}<$$

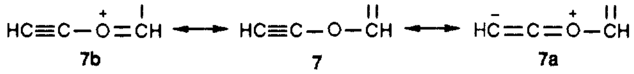
B

$$\text{H}_3\text{C}\overset{1.419\ \text{Å}}{\text{———}}\text{O}_2\text{C–H} \quad \Delta = 0.044\ \text{Å} \quad \text{H}_2\text{C=CH}\overset{1.375\ \text{Å}}{\text{———}}\text{O}_2\text{C–H} \quad \Delta = 0.063\ \text{Å} \quad \text{HC}\equiv\text{C}\overset{1.312\ \text{Å}}{\text{———}}\text{O}_2\text{C–H}$$

$$\text{CH}_3\text{CH}_2\overset{1.528\ \text{Å}}{\text{———}}\text{CH}_3 \quad \Delta = 0.025\ \text{Å} \quad \text{H}_2\text{C=CH}\overset{1.503\ \text{Å}}{\text{———}}\text{CH}_3 \quad \Delta = 0.035\ \text{Å} \quad \text{HC}\equiv\text{C}\overset{1.468\ \text{Å}}{\text{———}}\text{CH}_3$$

Of special interest is the comparison of the structural features of the ester moiety in the acetylenic esters with those in the corresponding vinylic (**10**) and saturated (**11**) esters. The calculated (6-31G*) C–O bond lengths in **7**, **10**, and **11** are compared in Chart I with the corresponding experimental values. Chart I also includes similar data for the C–C bond lengths in the corresponding hydrocarbons.

The trend of considerable shortening of the C–O bond on changing the hybridization at the "alkyl" carbon from sp^3 to sp^2 and from sp^2 to sp is clearly evident both in the experimental (Chart IA) and in the theoretical (Chart IB) values. The discussion below is based on the theoretical values which change more regularly than the average experimental values. The effect of the change in the carbon hybridization is larger (both nominally and percentagewise) on going from sp^2 to sp hybridization than on going from sp^3 to sp^2 hybridization. Thus, the C–O bond length shortens by 0.044 Å (3.1%) on going from sp^3 to sp^2 and by 0.063 Å (4.6%) on going from sp^2 to sp. As seen in Chart IB the calculated changes in the C–O bond lengths on going from sp^3 to sp hybridization are slightly larger than the corresponding changes in the calculated C–C bond lengths. This seems reasonable because the changes in the carbon–carbon bond lengths are due exclusively to hybridization effects[4] whereas overlap between the carbon–carbon π-bond(s) of the ester alkenyl or alkynyl groups and the lone pair(s) on oxygen may cause further bond shortening in the C–O bonds. This π-overlap can be described by resonance structures such as **7a** and **7b**.



7b **7** **7a**

Examination of the Mulliken population analysis (Figure 5) of the total and π-charges in **7** and comparison with **10** and **11** shed light on the contributions of these resonance structures to the electronic structures of alkynyl esters.[25] The calculated total charges in **7** reveal strong charge polarization mainly around the ester functionality. The net charges on the ester OC═O unit and on the acetylenic unit are −0.31 and +0.31 electron, respectively, and the dipole moment of **7** is 1.53 D (6-31G*). A similar and even a larger polarization in the total charge is also found in **10** and **11** (the 6-31G* calculated dipole moments are 1.69 and 1.98 D, respectively), so that in this respect there are no marked differences between **7**, **10**, and **11**. The relatively large negative charge of −0.18 electron at the β-acetylenic carbon (i.e., C_1) of **7** is consistent with the fact that in the ^{13}C NMR spectra of acetylenic esters this carbon absorbs at 20–30 ppm higher field than the α-acetylenic carbon (i.e., C_2).[2] A glance at the π-charges shows that the accumulation of negative charge at C_1 is mainly a σ-effect; only 0.06 electron can be described as being transferred to this carbon via resonance structure **7a** (in **10** such π-charge transfer is even smaller, 0.04 electron). The fact that in **7** the alkyl oxygen donates 0.18 electron into the π-framework (Figure 6) shows that resonance structures such as **7a** and **7b** contribute significantly to the total electronic wave function of **7**. Comparison of the calculated π-charges in **7**, **10**, and **11** reveals a similar behavior for the three esters, with the π-charge being transferred from the ester alkyl oxygen being 0.18–0.21 electron. Thus, although the ethynyl substituent is more strongly electron-withdrawing than ethenyl or methyl, this has little effect on the ability of the lone pairs on oxygen to participate in resonance with the carbonyl group (e.g., **7b**).

Additional information on the importance of resonance structures such as **7a** and **7b** may be obtained from the magnitude of the barrier to rotation around the alkyl C–O bond.[26] A higher rotation barrier is usually interpreted as indicating a higher double bond character between the alkyl oxygen and the acyl carbon, and thus a more important contribution of resonance structure **7b**[26] (a different interpretation was recently suggested to account for the magnitude of the barriers to rotation around ester and amide bonds[20a]). We calculate at 6-31G* that the barrier to rotation around the O—C═O bond in **7** [i.e., the energy difference between **7S** and **7P** (P = perpendicular): in **7P** the $C_2O_3C_4O_5$ dihedral angle is held at 90° and the other parameters are fully optimized] is 9 kcal mol^{-1}, indicating a substantial contribution of structure **7b**. As expected according to **7b** the alkyl C—O bond in **7P** is longer than in **7S**, but in contrast to expectation the C═O bond in **7P** is slightly shorter than in **7S** (for a similar observation, see ref 20a). We note however that the barrier to rotation in **7** is significantly lower than the corresponding rotation barrier of 12.8 kcal mol^{-1} (calculated with the same basis set) in methyl formate (**11**).[20a] The smaller rotation barrier in **7** compared with that in **11** can be attributed to electron donation from the alkyl oxygen to the electron-withdrawing ethynyl group as in **7a**, which reduces its ability to conjugate with the carbonyl group. Similar electron donation is not possible in **11**. This rationalization is consistent with the calculated accumulation of negative charge at the β-acetylenic carbon and the upfield shift of this specific carbon in the ^{13}C NMR[2] (see above).

b. Thermodynamic Stabilities. At present, experimental data on the thermodynamic stabilities of alkynyl esters are not available, and therefore, theory was used to obtain such information. Equations 1–3 give the energy changes for the hydrolysis of the parent alkynyl, alkenyl, and alkyl esters, respectively.

$$\underset{\mathbf{7}}{\text{HCOOC}\equiv\text{CH}} + \text{H}_2\text{O} \rightarrow \text{HCO}_2\text{H} + \text{HC}\equiv\text{COH} \qquad (1)$$

ΔE(kcal mol^{-1}) = −8.9 (6-31G*), −6.4 (MP2/6-31G*//6-31G*), −7.3 (MP3/6-31G*//6-31G*)

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[25] The use of Mulliken population analysis for calculating charge distributions has well-known drawbacks.[21] However, we believe that in the current context it is useful because of the following: (a) we reach the same conclusions by using either the 3-21G or the 6-31G* basis sets; (b) we compare three esters (**7**, **10**, and **11**) which are closely related electronically and structurally, and in such comparisons the Mulliken analysis is expected to reproduce at least the qualitative electronic trends.[21]

[26] Wheland, G. W. *Resonance in Organic Chemistry*; Wiley: New York, 1955; p 160. Streitwieser, A., Jr.; Heathcock, C. H. *Introduction to Organic Chemistry*, 3rd ed.; Macmillan Publ.: New York, 1985; pp 476–477. See, however, ref 20a for a different interpretation.

$$\underset{\textbf{10}}{HCOOCH{=}CH_2} + H_2O \rightarrow HCO_2H + H_2C{=}CH(OH) \quad (2)$$

ΔE(kcal mol^{-1}) = -4.3 (6-31G*), -2.8 (MP2/6-31G*//6-31G*)

$$\underset{\textbf{11}}{HCOOCH_3} + H_2O \rightarrow HCO_2H + CH_3OH \quad (3)$$

ΔE(kcal mol^{-1}) = 1.5 (6-31G*), 3.6 (MP2/6-31G*//6-31G*)

The calculations show that while the hydrolysis of **11** is slightly endothermic it is exothermic for **10** and more strongly so for **7**. This suggests that as the hybridization of the alkyl carbon changes from sp^3 to sp^2 to sp the thermodynamic stability of the ester decreases, the acetylenic ester being the least stable in accord with experimental observations.[1-3]

The frontier orbitals of **7** are also of interest. As expected, the HOMO and the LUMO of **7** (Figure 6) and of the vinyl analogue **10** have similar shapes. The HOMO is composed mainly of the antibodning combination between the acetylenic π-bond and the 2P lone pair or oxygen. The LUMO is concentrated, as expected, on the carbonyl group, but it includes significant contributions from the C≡C—O unit. An interesting difference in the shapes of the LUMO's of **7** and **10** is that in **7** the wave function is much more localized at the carbonyl than in **10** where mixing with the π-orbitals of the C=C—O fragment is more significant. Comparison of the energies of the HOMO and LUMO of **7** and **10** indicates that the relative hydrolysis rates of alkynyl and alkenyl esters cannot be understood in terms of their frontier orbitals. Thus, although the LUMO of **7** lies only 2.3 kcal mol^{-1} (6-31G*) lower in energy than the LUMO of **10**, the nucleophilic (i.e., basic or neutral) hydrolysis rates of alkynyl and alkenyl esters differ markedly.[27] This point is even more pronounced for the electrophilic (i.e., acidic) hydrolyses where it was found that alkynyl esters hydrolyze faster than alkenyl esters[27] although the HOMO of **7** lies 24.6 kcal mol^{-1} (6-31G*) lower in energy than the LUMO of **10**.[27] In acidic hydrolysis the relative energies of the intermediate carbocations (i.e., vinyl vs alkyl) probably plays the major role in dictating their relative hydrolysis rates. Further theoretical studies aimed at elucidating the mechanistic details of the hydrolysis reactions of alkynyl esters are in progress.

c. Comparison of the Theoretical and Experimental Structure of Vinyl Formate (10). Finally, since we have calculated the structure of **10** at 6-31G*, a higher level of theory than was previously available,[28,29] it is appropriate to comment on the performance of the calculations for this particular ester. We find that the 6-31G* molecular structure of **10** (Figure 4) is in very good agreement with the experimental structure determined by a combination of electron diffraction, microwave, and infrared data.[29] The preferred conformation of **10** is calculated to be (as also found experimentally[29]) sp,ap, i.e., the $C_2O_3C_4O_5$ and the $C_1C_2O_3C_4$ dihedral angles are 0° and 180°, respectively, as shown in Figure 7. The sp,sp conformation (i.e., where these dihedral angles are both 0°) is 2.4 kcal mol^{-1} (MP2/6-31G*//6-31G*) higher in energy. The ap,ap and ap,sp conformations are 4.7 and 7.4 kcal mol^{-1} (MP2/6-31G*//6-31G*), respectively, less stable than the sp,ap ground-state conformation. As expected,[20a] these energy differences are larger at 6-31G*/6-31G*. All the bond lengths of interest, i.e., $C_1{=}C_2$, $C{=}C_2{-}O_3$, and $O_3{-}C_4$, are calculated to be shorter by ca. 0.02 Å than those determined experimentally, as expected when using single determinant theory.[21] For example, the $C_1{=}C_2$, the $C{=}C_2{-}O_3$, and the $O_3{-}C_4$ bond lengths are 1.311 Å (6-31G*, 1.331 Å experimental), 1.375 Å (6-31G*, 1.397 Å experimental), and 1.327 Å (6-31G*, 1.350 Å, experimental), respectively. A similarly good agreement between theory and experiment is found for methyl formate (**11**), where the 6-31G* calculated $H_3C{-}O$ and $O{-}C{=}O$ bond lengths are both by ca. 0.02 Å shorter than the experimental distances.[30] The good agreement between the calculations and the experimental geometries for **10** and **11** (except for the expected corrections due to neglect of correlation energy) emphasizes the unusual discrepancy discussed above, between the C≡C and C≡C—O bond lengths calculated for **7** and the corresponding experimental bond

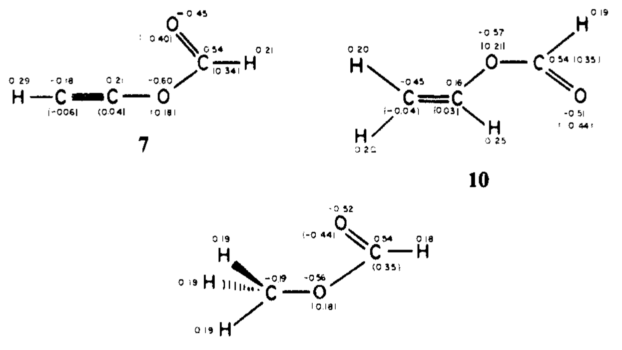

Figure 5. Total and π-charges (6-31G*) in esters **7**, **10**, and **11**. The values given in parentheses are the π-charges.

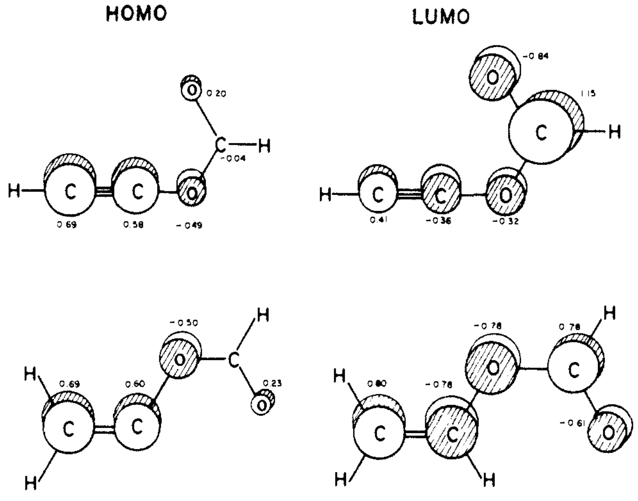

Figure 6. A schematic drawing of the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO, respectively) of **7** and **10**. The values given are the calculated 6-31G* orbital coefficients.

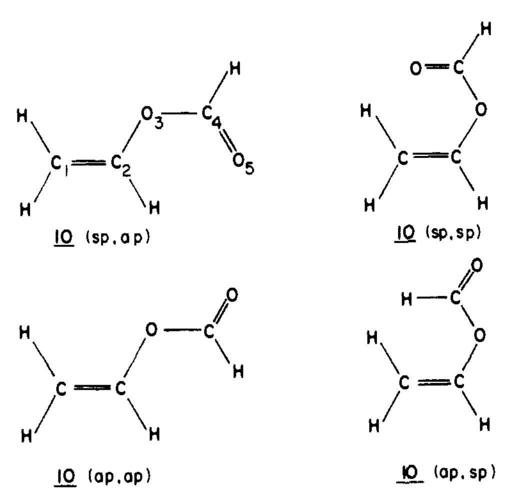

Figure 7. Calculated conformations of vinyl formate (**10**).

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distances in **4**. Further experimental, as well as theoretical, studies are needed to clarify the reasons for the discrepancy.

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Registry No. Propynyl *p*-nitrobenzoate, 113779-41-2; hydroxyacetylene, 32038-79-2; ethynyl formate, 123812-75-9; propynyl formate, 123812-74-8; ethynyl acetate, 83313-98-8; vinyl formate, 692-45-5; methyl formate, 107-31-3.

Hexaazaoctadecahydrocoronene.[†] Structural and Physical Properties of [HOC]^n (n = 0, 1+, 2+, 3+, 4+)

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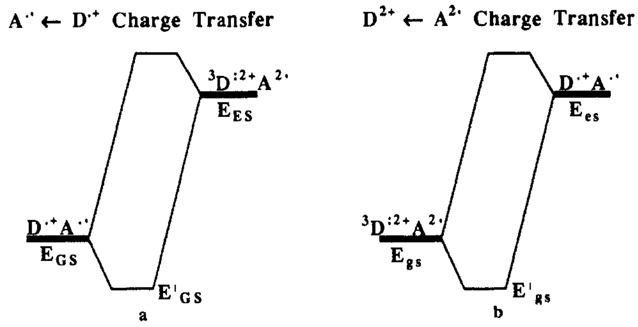
Abstract: Hexaazaoctadecahydrocoronene and its mono-, di-, tri-, and tetracations, [HOC]^n (n = 0, 1+, 2+, 3+, 4+), have been prepared and characterized by X-ray diffraction, EPR, magnetic susceptibility, and electronic and vibrational spectroscopies. HOC, [HOC]$^{\bullet+}$[BF$_4$]$^-$, [HOC]$^{\bullet+}$[TCNE]$^{\bullet-}$ (TCNE = tetracyanoethylene), [HOC]$^{\bullet+}$[F$_3$CSO$_3$]$^-$, [HOC]$^{2+}$\{[PF$_6$]$^-$\}$_2$, [HOC]$^{2+}$\{[BF$_4$]$^-$\}$_2$, [HOC]$^{2+}$\{[C(CN)$_3$]$^-$\}$_2$, [HOC]$^{2+}$\{C[C(CN)$_2$]$_3$\}$^{2-}$, [HOC]$^{2+}$\{Ni[S$_2$C$_2$(CF$_3$)$_2$]$_2$$^{\bullet-}$\}$_2$, [HOC]$^{\bullet3+}$\{[PF$_6$]$^-$\}$_3$, [HOC]$^{\bullet3+}$\{[SbF$_6$]$^-$\}$_3$, and [HOC]$^{4+}$\{[SbF$_6$]$^-$\}$_4$·MeCN have been studied by single-crystal X-ray diffraction. HOC and [HOC]$^{4+}$ have essentially equivalent C$_6$-ring C–C bond distances averaging 1.397 and 1.436 Å, respectively. Their average C$_6$-ring C–N distances are 1.416 and 1.318 Å, respectively. The dication, [HOC]$^{2+}$, has a distorted (Jahn–Teller) structure corresponding to coupled cyanine fragments with distinctly different short (1.395-Å) and long (1.471-Å) C$_6$-ring C–C and C–N (1.337- and 1.405-Å) bond distances. The 1+ and 3+ radical ions also show distorted structures, although the distortions are smaller than observed for the 2+ structure. The short C$_6$-ring C–C bond distances are 1.382 and 1.417 Å, and the long C$_6$-ring C–C bond distances are 1.444 and 1.439 Å, while the short C$_6$-ring C–N bond distances are 1.371 and 1.326 Å and the long C$_6$-ring C–N bond distances are 1.422 and 1.339 Å, respectively. Solid-state magnetic susceptibility measurements show that the n = 0, 2+, and 4+ compounds are diamagnetic and that the n = 1+ and 3+ salts are $S = {}^1/_2$ paramagnets that obey the Curie–Weiss expression between 2 and 320 K. The effective moments, μ_{eff}, and Curie–Weiss constants, θ, are 1.77 and 1.75 μ_B and θ = –3.3 and –0.9 K for the mono- and trications, respectively. The n = 1+ and 3+ radical cations are fluxional in solution. The EPR spectrum of [HOC]$^{\bullet+}$ in the fast-exchange limit (25 °C) shows that all protons and N's have the same hyperfine splitting (2.56 G, g = 2.003 15). In the slow-exchange limit (–90 °C), there are 2 sets of 12 equivalent protons (0.974 and 4.222 G) and 6 equivalent N's (2.595 G). This precludes the observation of a Jahn–Teller distortion in solution. The [HOC]$^{\bullet3+}$ ion is more fluxional in solution as it exhibits fast-exchange behavior at –60 °C [a(24H) = a(6 N) = 2.81 G; g = 2.0310]. EPR spectra of polycrystalline [HOC]$^{2+}$ salts show the presence of thermally accessible triplet species whose zero-field splitting parameters are $|D|$ = 0.0550 ± 0.0008 cm^{-1} and $|E|$ = 0.0024 ±0.0005 cm^{-1} and are appropriate for triplet states of less than 3-fold symmetry. The temperature dependence of the $\Delta M = \pm 2$ EPR absorption afforded the separation between the ground singlet state and the excited triplet state of the dication for a variety of [HOC]$^{2+}$ salts. For most counteranions, these separations are greater than 3 kcal/mol (1050 cm^{-1}, 0.13 eV). Solid-state magnetic susceptibility measurements for those [HOC]$^{2+}$ with singlet–triplet gaps less than 4.0 kcal/mol show increases in susceptibilities at higher temperatures, consistent with the presence of thermally populated triplet excited states. Magnetic susceptibility and single-crystal X-ray structures of the dication in the crystalline materials of this study are consistent with a singlet ground state. Molecular orbital (ab initio) calculations are in general agreement with the above results.

Scheme I



With guidance from a model proposed by H. M. McConnell,[1] stable triplet (S = 1) organic species have been deliberately designed[2,3] and synthesized as potential components of s/p-orbital-based molecular ferromagnets.[3,4] This goal has recently been achieved with the characterization of the donor–acceptor complex, DA, [Fe^{III}(C$_5$Me$_5$)$_2$]$^{\bullet+}$[TCNE]$^{\bullet-}$ as a molecular/organic bulk ferromagnet.[3,5] At the present time, the McConnell model provides a useful conceptual framework for understanding the stabilization of ferromagnetic coupling in this system. The essence of the model is that the energy of the D$^{\bullet+}$A$^{\bullet-}$ ground state (E_{GS}) is lowered to E'_{GS} by configurational mixing with the ^{3}D$^{:2+}$A^{2-} excited state[6a] (E_{ES}), thus stabilizing pairwise ferromagnetic coupling, Scheme Ia. Likewise, it is feasible that the energy of a ^{3}D$^{:2+}$A^{2-} ground state[6b] (E_{gs}) could also be lowered to E'_{gs} by configurational mixing with the D$^{\bullet+}$A$^{\bullet-}$ excited state (E_{es}) to stabilize ferromagnetic coupling, Scheme Ib. Although triplet ^{3}[Fe^{III}(C$_5$Me$_5$)$_2$]$^{:2+}$ is an unknown species, admixing of the D$^{:2+}$A^{2-} virtual state with the ground state was invoked to explain the

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[†] The ACS Editorial Office suggests dodecahydrohexaazacoronene as a more appropriate name (due to the lower hydrogen content when nitrogen replaces carbon).

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