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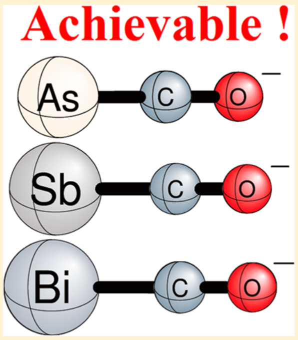
The Cyanate and 2-Phosphaethynolate Anion Congeners ECO^- (E = N, P, As, Sb, Bi): Prelude to Experimental Characterization

Yunxiang Lu,*,[†] Hui Wang,[‡] Yaoming Xie,[§] Honglai Liu,[†] and Henry F. Schaefer*,[§]

[†]Key Laboratory for Advanced Materials and Department of Chemistry, East China University of Science and Technology, Shanghai, 200237, China

[‡]School of Physical Science and Technology, Southwest Jiaotong University, Chengdu, 610031, China

[§]Center for Computational Quantum Chemistry, University of Georgia, Athens, Georgia 30602, United States



ABSTRACT: Pioneering synthetic research by the groups of Grutzmacher and Goicoechea have made possible the preparation of 2-phosphaethynolates (PCO^-). The obvious question arises: can progress be made toward $AsCO^-$, $SbCO^-$, and $BiCO^-$? Here the properties of all five anion congeners ECO^- (E = N, P, As, Sb, Bi) were systematically investigated using ab initio coupled-cluster methods with correlation-consistent basis sets cc-pVXZ (X = D, T, Q). These anions exhibit linear structures with significant natural bond orbital negative charge on both the E and O atoms. These species should react with electrophiles via attack at either center. On going from nitrogen to bismuth, with the atomic radius increasing, the bond between E and C becomes weaker, while the C−O bond tends to be slightly stronger. By the time one gets to $BiCO^-$, the C−O bond distance is 1.181 Å, indicating a very strong double bond. Relative to the PCO^- anion, which is reactive toward several unsaturated compounds, the As/Sb/BiCO$^-$ anions may undergo cycloaddition more readily with unsaturated substrates. The dissociation energy of the E−C bond, except for that of NCO^-, is predicted to be much less than that of the C−O bond. These dissociation energies are 76 kcal/mol (P^-−CO), 58 kcal/mol (As^-−CO), 37 kcal/mol (Sb^-−CO), and 28 kcal/mol (Bi^-−CO). Even the $BiCO^-$ anion should be achievable in the laboratory. The vibrational frequencies for these anions are predicted, and our results should assist in the experimental characterization and exploration of the heavier congeners ECO^-.

1. INTRODUCTION

The 2-phosphaethynolate anion (PCO^-), a phosphorus-containing analogue of cyanate ion (NCO^-), was first prepared in 1992 by Becker, Schwarz, Seidler, and Westerhausen[1] as a lithium salt. Nine years later Westerhausen and co-workers[2] reported the syntheses of the magnesium, calcium, strontium, and barium bis 2-phosphaethynolates. In 2011, much higher yields of this anion were achieved in the synthesis by Grutzmacher and co-workers[3] of two novel salts from $NaPH_2$ and CO under high-pressure conditions. Jupp and Goicoechea[4] have very recently reported a more convenient synthesis of the 2-phosphaethynolate anion via direct combination of CO with a K_3P_7 solution. The new synthesis of Jupp and Goicoechea facilitated the study of the reactions of PCO^- with diphenylketene and related compounds to produce interesting [2 + 2] cycloaddition chemistry.[4] The cycloaddition reactivity and, most importantly, the “P” transfer properties of PCO^- have been explored very recently by Grutzmacher et al.[5−7] PCO^- is of interest as a pseudo halide[8] and for examining multiple bonds between carbon and the main group elements.[9] Jupp and Goicoechea’s X-ray diffraction study[4] of single crystals of [K([18]crown-6)][PCO] revealed that this anion exhibits a linear structure with a formal triple bond between the phosphorus and carbon atoms (1.579(3) Å). Becker and Hubler’s spectroscopic and crystallographic studies of the valence isoelectronic PCS^- anion also disclosed a linear structure with a P≡C triple bond (1.555(11) Å).[10] These successes in transitioning from NCO^- to PCO^- raise the obvious question: can heavier congeners of PCO^- be made?

There is a very substantial body of experimental research that has been carried out on the parent cyanate anion NCO^-. References 11−16 are by no means exhaustive. Particularly noteworthy are (a) Gruebele, Polak, and Saykally’s velocity modulation infrared study[14] of NCO^-, (b) the photoelectron spectroscopic study by Neumark and co-workers,[15] and (c) the 2010 microwave spectroscopic research of McCarthy, Thaddeus, and co-workers.[16] The latter sets the stage for the future identification of NCO^- in interstellar space. Among the many theoretical studies of NCO^-, those of Pak, Woods, and Peterson[17] and Leonard and co-workers[18] are particularly noteworthy. The established body of research on NCO^- provides stringent tests on our theoretical predictions for the heavier congeners PCO^-, $AsCO^-$, $SbCO^-$, and $BiCO^-$.

It is very important to note that the $AsCO^-$ anion has been observed via matrix isolation infrared spectroscopy. That research by Zhang, Dong, and Zhou[19] is, to our knowledge, the first success in the observation of the heavier PCO^- congeners. The present research presses on to reliable theoretical predictions for the entire family NCO^-, PCO^-, $AsCO^-$, $SbCO^-$, and $BiCO^-$.

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2. THEORETICAL METHODS

The geometries of the anions under study were optimized by means of coupled-cluster theory incorporating single and double excitations with perturbative triple excitations [CCSD(T)].[20−22] The harmonic vibrational frequencies were determined with the same methods by evaluating the second derivatives of the potential energy surface (PES).

For the C, N, O, and P atoms, the Dunning−Woon correlation-consistent basis sets[23,24] cc-pVXZ (X = D, T, Q) were used. The Stuttgart−Cologne multiconfiguration Dirac−Hartree−Fock (MCDHF) adjusted effective core potentials (ECP) and the corresponding correlation-consistent basis sets cc-pVXZ-PP were employed for the As, Sb, and Bi atoms.[25−27] Within the ECPs, 10 core electrons ($1s^22s^22p^6$) are embodied in the effective core potential for As, 28 core electrons ($1s^22s^22p^63s^23p^63d^{10}$) for Sb, and 60 core electrons ($1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}4f^{14}$) for Bi. In addition, for the lighter atoms the inner obitals were frozen in the correlated wave functions; that is, the 1s-like molecular orbital (MO) was frozen (held doubly occupied in the coupled-cluster procedures) for the C, N, and O atoms, and the phosphorus 1s2s2p-like MOs were frozen. Because the d^{10} electron correlation is significant for the As ($3d^{10}4p^3$), Sb ($4d^{10}5p^3$), and Bi ($5d^{10}6p^3$) atoms, only the 3s3p, 4s4p, and 5s5p orbitals were frozen for As, Sb, and Bi, respectively. The coupled-cluster computations were carried out with the CFOUR program packages.[28]

The natural bond orbital (NBO) atomic charges[29] and Wiberg bond orders (WBI)[30] for the studied anions were evaluated with the density functional theory (DFT) method (BP86/cc-pVQZ),[31,32] and these computations were preformed via the Gaussian 09 suite of programs.[33]

3. RESULTS AND DISCUSSION

Electronic Structures and Molecular Obitals. The cyanate ion and CO_2 are isoelectronic species and thus have similar linear geometries (Figure 1) and similar electronic structures. The cyanate ion has the following electronic configuration:

$$[\text{core}]4\sigma^25\sigma^26\sigma^21\pi^47\sigma^22\pi^4$$

where [core] = $1\sigma^22\sigma^23\sigma^2$ denotes three lowest-lying 1s-like core MOs for the N, C, and O atoms. The electronic configuration of the 2-phosphaethynolate anion is described as

$$[\text{core}]6\sigma^27\sigma^28\sigma^22\pi^49\sigma^23\pi^4$$

where [core] = $1\sigma^22\sigma^23\sigma^24\sigma^25\sigma^21\pi^4$, including the 1s2s2p-like MOs for the P atom, as well as the 1s-like MOs of C and O. The valence electron configurations of other three anions ECO^- (E = As, Sb, Bi) are analogous, that is, four σ orbitals and two pairs of π orbitals.

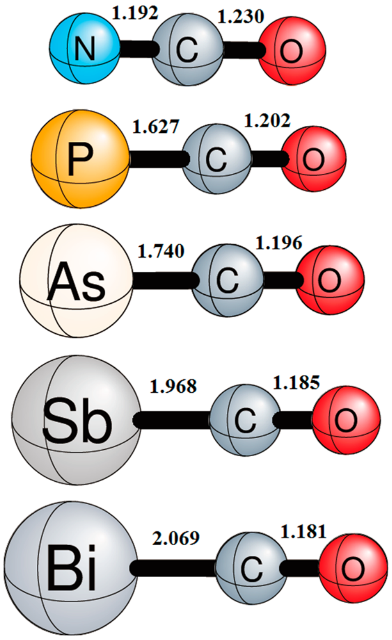

Figure 1. Optimized geometries at the highest level of CCSD(T)/cc-pVQZ for the five ECO^- anions. Distances are in angstroms.

The occupied valence MOs for the cyanate and 2-phosphaethynolate anions are displayed in Figure 2. As may be seen, the highest occupied molecular orbital (HOMO) and HOMO−1 orbitals of PCO^- make up the degenerate 3π MO, and each component ($3\pi_x$ or $3\pi_y$) is a nonbonding orbital. The HOMO−3 and HOMO−4 form the 2π bonding MO. The four σ-type orbitals (HOMO−2, HOMO−5, HOMO−6, and HOMO−7) include two σ bonds (P−C and C−O) and two σ lone pairs (on P and O atoms). Thus, both the P−C and C−O bonds in the anion have formal double bonds, similar to its

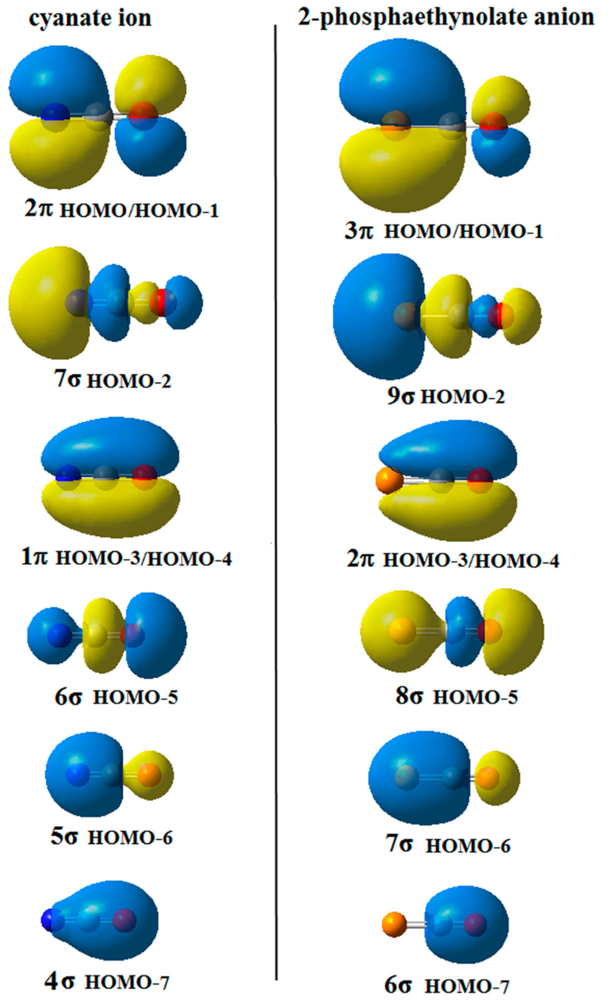

Figure 2. Occupied valence molecular orbitals of cyanate and 2-phosphaethynolate anions.

Table 1. Bond Distances (Å) of the Five ECO$^-$ Anions Predicted by the CCSD(T) and BP86 Methods

	CCSD(T)			BP86		
	cc-pVDZ	cc-pVTZ	cc-pVQZ[a]	cc-pVDZ	cc-pVTZ	cc-pVQZ
r(E−C)						
[N−C−O]$^-$	1.210	1.195	1.192 (1.195(11))[b]	1.213	1.201	1.200
[P−C−O]$^-$	1.647	1.631	1.627 (1.579(3))[c]	1.648	1.634	1.632
[As−C−O]$^-$	1.764	1.746	1.740	1.770	1.760	1.761
[Sb−C−O]$^-$	1.995	1.979	1.968	1.995	1.986	1.988
[Bi−C−O]$^-$	2.107	2.084	2.069	2.111	2.096	2.100
r(C−O)						
[N−C−O]$^-$	1.243	1.233	1.230 (1.180(11))[b]	1.245	1.236	1.235
[P−C−O]$^-$	1.216	1.207	1.202 (1.212(4))[c]	1.220	1.212	1.210
[As−C−O]$^-$	1.210	1.200	1.196	1.215	1.206	1.203
[Sb−C−O]$^-$	1.200	1.191	1.185	1.206	1.198	1.194
[Bi−C−O]$^-$	1.196	1.188	1.181	1.202	1.195	1.190

[a] The values in parentheses were taken from experimental crystal structures. [b] Reference 34, AgNCO. [c] Reference 4, [K([18]crown-6)]-PCO.

valence isoelectronic O=C=O species. Two resonance structures of the 2-phosphaethynolate anion (P≡C−O$^{\ominus}$ and $^{\ominus}$P=C=O) were mentioned by Jupp and Goicoechea, and their [2 + 2] cyclization experiments suggest the latter structure for this anion.[4]

The energy gaps between HOMO and lowest unoccupied molecular orbital (LUMO) obtained with the BP86/cc-pVQZ method for the five anions amount to 6.26eV (NCO$^-$), 4.23eV (PCO$^-$), 3.79eV (AsCO$^-$), 3.10eV (SbCO$^-$), and 2.89eV (BiCO$^-$). This suggests that the cyanate ion has stability and resistance to charge transfer, while for other ECO$^-$ anions the energetic favorability decreases and the polarizability increases going down the periodic table.

Structures and Charge Distributions. The bond distances E−C and C−O for the five anions predicted with different theoretical methods are reported in Table 1, and the optimized geometries at the highest level CCSD(T)/cc-pVQZ are depicted in Figure 1. All the anions exhibit linear structures, consistent with the NCO$^-$ and PCO$^-$ X-ray crystal structures.[4,34] With the CCSD(T) method, the estimated E−C and C−O bond distances become shorter when the size of the basis set increases. However, the differences of bond distances between cc-pVTZ and cc-pVQZ are not too large (within 0.015 Å). In the following discussion we will focus on the cc-pVQZ results. Table 1 shows that the BP86 bond distances are predicted to be 0.01−0.03 Å longer than the CCSD(T) results.

At the CCSD(T)/cc-pVQZ level of theory, the N−C bond distance in the cyanate ion is 1.192 Å, somewhat longer (by ~0.05 Å) than that for typical neutral cyanide molecules RCN.[35] Similarly, the P−C distance (1.627 Å) in the 2-phosphaethynolate anion is predicted to be longer than that for free phosphaalkynes RCP (1.522−1.558 Å).[36] The C−O distance in the NCO$^-$ and PCO$^-$ anions is estimated to be 1.230 and 1.202 Å, respectively, which is in the range of a typical C=O double bond. However, the predicted C−O bond distance for isolated NCO$^-$ does not compare well with that in the crystal structure of silver cyanate AgNCO (1.180(11) Å),[34] which may be ascribed to crystal packing forces.

Table 2 shows that both the N/P and O atoms in the NCO/PCO$^-$ anions carry significant negative charge in the NBO picture. This is not consistent with the traditional valence structures $^{\ominus}$N=C=O and $^{\ominus}$P=C=O, which place the entire negative charge on the N/P atom. The NBO negative charge on the E atoms (E = P, As, Sb, Bi) becomes less negative monotonically (after N) going down the periodic table, and for the BiCO$^-$ anion, the Bi and O atoms possess almost the same negative charge (~0.57). Consequently, these anions may react with electrophiles via attack at either center, similar to the cyanate ion.

Table 2. Natural Bond Orbital (NBO) Atomic Charges (a.u.) and Wiberg Bond Indices (WBI) of the Five ECO$^-$ Anions Predicted with the BP86/cc-pVQZ Method

	q_E	q_C	q_O	WBI(E−C)	WBI(C−O)
[N−C−O]$^-$	−0.78	0.50	−0.72	2.45	1.52
[P−C−O]$^-$	−0.45	0.06	−0.61	2.23	1.66
[As−C−O]$^-$	−0.50	0.09	−0.60	2.14	1.70
[Sb−C−O]$^-$	−0.51	0.09	−0.58	1.96	1.76
[Bi−C−O]$^-$	−0.56	0.14	−0.57	1.86	1.80

Here it is worth mentioning that the protonation of the terminal atoms of NCO$^-$ produces two isomers, isocyanic acid (HNCO) and cyanic acid (NCOH),[37] and these two isomers exhibit quite different Lewis structures (HN=C=O and N≡C−OH). In the crystal structure of AgNCO,[34] the N−C bond distance was determined to be 1.195(11) Å, close to our predicted value (1.192 Å). The reaction of Na(OCP) with silyl triflates produced both the R_3Si−O−C≡P and R_3Si−P=C=O isomers. The former is the kinetic product, while the latter is the thermodynamically favored isomer.[38] In the present research the bare anions ECO$^-$, with negative charge on both E and O atoms, might be thought to have a hybrid structure of the two resonance forms ($^{\ominus}$E=C=O and E≡C−O$^{\ominus}$). However, the latter valence structure seems unrealistic for the As, Sb, and Bi structures in light of the length of their C−O bonds, all comparable to that for the prototypical C=O bond in formaldehyde (1.21 Å). Therefore, the molecular structures of the heavier congeners have larger contributions from the valence structures $^{\ominus}$E=C=O. We also studied the triplet states of these anions, but the E−C bonds usually break during the optimizations. Thus, the radical character should be negligible for these anions.

The predicted C−O bond distances form a beautiful monotonic sequence: 1.230 Å (NCO$^-$), 1.202 Å (PCO$^-$), 1.196 Å (AsCO$^-$), 1.185 Å (SbCO$^-$), and 1.181 Å (BiCO$^-$). By the time we get to the bismuth compound, it is apparent that the C−O distance is significantly shorter than a traditional double bond. However, the C−O distance in BiCO$^-$ is still significantly longer than the r_e = 1.128 Å value found for

Table 3. Bond Dissociation Energies (kcal/mol) of the Five ECO^- Anions Predicted with the CCSD(T) and BP86 Methods

	CCSD(T)			BP86		
	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pVDZ	cc-pVTZ	cc-pVQZ
BDE(E^-−CO)						
$[N{-}C{-}O]^{-a}$	157.98	157.07	154.74	180.19	170.69	165.34
$[P{-}C{-}O]^-$	71.95	75.54	75.98	92.63	90.00	87.81
$[As{-}C{-}O]^-$	52.61	58.21	58.13	72.40	69.88	67.00
$[Sb{-}C{-}O]^-$	29.56	35.75	37.16	50.05	48.90	46.38
$[Bi{-}C{-}O]^-$	19.32	27.19	28.32	39.84	40.45	37.30
BDE(EC^-−O)						
$[N{-}C{-}O]^-$	118.21	125.96	129.10	145.72	145.37	153.24
$[P{-}C{-}O]^-$	146.99	155.75	158.66	175.49	175.90	182.85
$[As{-}C{-}O]^-$	150.14	157.97	161.13	178.36	178.00	177.99
$[Sb{-}C{-}O]^-$	158.66	167.14	170.22	186.43	187.03	186.55
$[Bi{-}C{-}O]^-$	160.71	168.66	171.86	188.88	189.14	188.91

[a] Note that this is not a physical prediction as the isolated nitrogen atom does not bind an electron.

diatomic CO in the gas phase. As is often the case, the largest bond distance change occurs between the first (N) and second (P) rows of the periodic table.

Bond Dissociation Energies. The thermodynamic stability of these anions may be associated with the bond dissociation energies (BDEs). Two sets of BDEs of anion were determined here via the following:

$$ECO^-(^1\Sigma^+) \rightarrow E^-(^3P) + CO(^1\Sigma^+)$$

$$BDE(E^- {-} CO) = E_{E^-} + E_{CO} - E_{ECO^-} \qquad (1)$$

$$ECO^-(^1\Sigma^+) \rightarrow EC^-(^1\Sigma^+) + O(^3P)$$

$$BDE(EC^- {-} O) = E_{EC^-} + E_{O} - E_{ECO^-} \qquad (2)$$

Table 3 shows the BDEs for the five anions computed with the CCSD(T) and BP86 methods. Usually, the BDEs become greater with the increase in the size of the basis set. The BDE differences between cc-pVTZ and cc-pVQZ are modest (within 3.20 kcal/mol), and we will discuss the CCSD(T)/cc-pVQZ results. On going from N to Bi, the E^-−CO BDEs are predicted to decrease, confirming that the E−C bond becomes weaker with the increase in the atomic radius of E. In harmony, the WBI (Table 2) for the E−C bond becomes smaller, that is, from 2.45 (E = N), 2.23 (P), 2.14 (As), 1.96 (Sb), to 1.86 (Bi). In this connection, compared with the PCO anion that shows reactivity toward several unsaturated compounds,[4] the As/Sb/$BiCO^-$ anions may undergo [2 + 2] cycloaddition more readily with unsaturated substrates. Note that the Sb−C and Bi−C bond dissociation energies could be comparable to metallic cluster bonding interactions, which may be helpful for preparing and characterizing these anions. In contrast, the EC^-−O BDEs become slightly larger with the increasing atomic radii of E, consistent with the results for the C−O bond distances (Figure 1). Accordingly, the WBI values for the C−O bonds for the ECO^- anions are predicted to be 1.52 (E = N), 1.66 (P), 1.70 (As), 1.76 (Sb), and 1.80 (Bi).

The cyanate ion has the largest E^-−CO BDE and smallest EC^-−O BDE among the five anions, and its (unphysical, see footnote to Table 3) E^-−CO BDE value (154.8 kcal/mol) is greater than its EC^-−O BDE value (129.1 kcal/mol). In contrast, the E^-−CO BDE values for other four anions are considerably smaller than their EC^-−O BDE values. This demonstrates that in the cyanate ion the C−O bond is more easily broken than the N−C bond, while in the other four anions the C−O bond is stronger than the E−C bond. Accordingly, the cyanate ion has the largest E−C bond index (2.45) and the smallest C−O bond index (1.52) among the five anions.

Vibrational Frequencies and Infrared Intensities. The harmonic vibrational frequencies for the ECO^- anions predicted with the CCSD(T)/cc-pVQZ method are reported in Table 4. For the cyanate ion, the most intense infrared frequency (2188 cm^{-1}) corresponds to the N−C−O asymmetric stretching mode. The next most intense fundamental frequency (629 cm^{-1}) is the bending mode. The symmetric stretching mode (1232 cm^{-1}) carries the least infrared intensity. The ν_3 fundamental for NCO^-, assigned to the CN stretch, was determined by Gruebele, Polak, and Saykally[14] to be 2124 cm^{-1} from velocity modulation infrared spectroscopy. This suggests a rather small degree of anharmonicity (64 cm^{-1}) for the asymmetric stretch. For the other four anions, the intense infrared feature (~1800 cm^{-1}) is the E−C−O asymmetric stretch, similar to that for the cyanate ion. However, the other two (bending and symmetric stretch) vibrational modes are predicted to have low infrared intensities. In the experimental infrared study by Zhang, Dong, and Zhou[19] of the $AsCO^-$ anion, the observed IR band at 1756.4 cm^{-1} was assigned to the C−O stretching vibration. Zhou's matrix isolated fundamental frequency lies 62 cm^{-1} below our harmonic frequency, consistent with our comparison for NCO^-.

Table 4. Harmonic Vibratonal Frequencies (cm^{-1}) and Infrared Intensities (km/mol, in parentheses) for the Five ECO^- Anions at the CCSD(T)/cc-pVQZ Level

	bending[a]	symmetric stretching	asymmetric stretching
$[N{-}C{-}O]^-$	629 (114)	1232 (79)	2188 (1021)
$[P{-}C{-}O]^-$	504 (50)	807 (8)	1838 (1615)
$[As{-}C{-}O]^-$	460 (5)	623 (<1)	1818 (1121)
$[Sb{-}C{-}O]^-$	403 (8)	503 (0)	1819 (1285)
$[Bi{-}C{-}O]^-$	372 (13)	430 (<1)	1810 (1388)

[a] The IR intensities for the 2-fold degenerate bending mode refer to one component.

4. CONCLUSIONS

In this work, the equilibrium geometries, dissociation energies, and vibrational frequencies of ECO^- (E = N, P, As, Sb, Bi) were systematically studied at the CCSD(T) level of theory with cc-pVDZ, cc-pVTZ, and cc-pVQZ basis sets. A standard DFT method (BP86) was also used for comparison. It was found that both the E and O atoms carry significant NBO negative charge, indicating that these anions are ambidentate with two nucleophilic centers. Going down the periodic table (increase of atomic radius), the E−C bond becomes weaker monotonically, and the C−O bond tends to be slightly stronger. Therefore, compared with PCO^-, which is reactive toward several unsaturated compounds, the As/Sb/$BiCO^-$ anions may undergo cycloaddition more readily with unsaturated substrates. For the cyanate ion, the dissociation energy of the N−C bond is predicted to be greater than that of the C−O bond, contrary to the other four anions. In fact, the NCO^- anion shows the largest E−C bond order and the smallest C−O bond order among the five studied anions.

Although the Sb^-−CO (37 kcal/mol) and Bi^-−CO (28 kcal/mol) dissociation energies are modest, the first step of preparation and identification via matrix isolation IR spectroscopy should be achievable. We hope that the present research will motivate efforts to prepare $SbCO^-$ and $BiCO^-$ in the laboratory. From the predicted CO removal energies, it seems likely that the bismuth species will be the most reactive.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: yxlu@ecust.edu.cn. (Y.L.)
*E-mail: qc@uga.edu. (H.F.S.)

Notes

The authors declare no competing financial interest.

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