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Prediction of new organo-noble gas compounds by *ab initio* quantum chemical calculations

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The existence of three new, linear organo-noble gas molecules, HArCCH, HKrCCKrH and HKrCCXeH, incorporating one or two noble gas atoms into the acetylene framework, is predicted by *ab initio* quantum chemical calculations using different methods and basis sets. Their optimized bond lengths, stability, nature of bonding and the role of correlation energy, preferred dissociation channel as well as propensity to attack by electrophiles have been reported. The bonding in HArCCH is different from that in the other molecules. For molecules containing two noble gas atoms, a 90° dihedral mode involving the atoms and the HCCH internuclear axis, is the preferred stereochemical approach. However, a noble gas atom could not be inserted into the biphenyl molecule as well as between two benzene molecules.

In recent years, an interesting development in the chemistry of noble gases has taken place via the low-temperature, solid-state synthesis and characterization of noble-gas hydrides of the form HNgY[1,2] where Ng is a noble gas atom and Y is an electronegative atom or group. Examples of such compounds with varying Ng and Y are: HArF[2,3], HXeH[4], HXeCl[4], HXeBr[4], HKrOH of doubtful existence[5,6], HXeOH[4], HXeSH[7], HKrCN[8,9], HXeCN[8,9] and HXeNC[8,9]. These molecules dissociate into neutral species although their equilibrium structures have partially ionic charge transfer character, i.e. their bonding nature is like $(\text{H-Ng}^+)(\text{Y}^-)$ with the H-Ng bond essentially covalent and the Ng-Y bond largely ionic. Their intrinsic stability has been confirmed by both experimental studies and quantum chemical calculations. Under this broad class of hydrides, a new class of organo-noble gas compounds has also been predicted by *ab initio* quantum chemical computations[10] and later synthesized at low temperatures[11,12]. These are insertion compounds of a noble gas atom (xenon or krypton) into an unsaturated hydrocarbon or alcohol, e.g., HKrCCH, HXeCCH, $HXeC_6H_5$, $HXeOC_6H_5$ as well as polymeric species such as $H(XeC_2)_nXeH$, $n \geq 1$, whose stability was predicted to increase with n. Such organo-xenon and organo-krypton compounds are highly reactive and may serve as catalysts in low-temperature reactions[13]. The structure and dynamics of such compounds have been reviewed by Gerber[14]. Very recently, $HArC_4H$[15], $HArC_6H$[15], $Kr(-C{\equiv}CH)_4$[16], $Xe(-C{\equiv}CH)_4$[16], $Kr(-C{\equiv}CH)_6$[16] and $Xe(-C{\equiv}CH)_6$[16] have been predicted by *ab initio* quantum chemical calculations. Furthermore, a compound like $C_6H_5{-}Xe{-}C_6H_5$ has been reportedly prepared[17].

In view of the above developments, the objectives of the present investigations are: (i) To predict new organo-noble gas compounds such as HKrCCXeH, HKrCCKrH and HArCCH. Their optimized geometries, stabilization energies (with respect to both isolated atom components as well as realistic dissociation fragment components) and molecular electrostatic potential(ESP) maps are to be obtained by *ab initio* quantum chemical calculations. Note that HArCCH is considered to be unstable with respect to dissociation into H + Ar + CCH[15]; (ii) To consider the nature of bonding in these three molecules; (iii) To determine the preferred mode of insertion of two noble gas atoms simultaneously into the acetylene framework; and, (iv) To attempt the insertion of a noble gas atom in biphenyl as well as between two benzene molecules in both lateral and sandwich modes.

Methodology

The main *ab initio* quantum chemical methods employed were restricted Hartree-Fock theory (RHF), Moeller-Plesset second-order perturbation theory (MP2) and density functional theory (DFT) with B3LYP exchange-correlation functional, by using the GAMESS software package[18]. For graphical display, the MOLDEN[19] and MOLEKEL[20] software packages were employed. The choice of basis sets was decided by the available computer time and the sets for the noble gas atoms in GAMESS. Thus, the 6-311G++(3d, 3p, 1f) set was used for the argon compound, the DZV+** set for the krypton compounds and the 3-21G set for the xenon compounds including the mixed krypton-xenon compound. We feel that while larger basis sets would lead to more accurate numbers (along with somewhat larger basis set superposition errors as well), the qualitative conclusions reached by us about the stability, bonding and geometry of these predicted molecules are unlikely to change. Furthermore, in such studies it is the relative changes in the values of various quantities, which provide greater insights rather than the absolute values.

The combination of RHF, MP2 and DFT adopted here is an optimum basket of *ab initio* methods, which satisfactorily deal with exchange and correlation. Of these, DFT has been the most widely acceptable *ab initio* method for atoms, molecules, clusters as well as nano-systems and solids, ground as well as excited states, small as well as large energy differences. In particular, DFT has considerable interpretative power because its fundamental variable is the electron density and not the wave function. We have also performed CCSD(T) calculations on the molecules. However, of the six organo-noble gas molecules examined here (see below), CCSD(T) geometry optimizations converged only for HKrCCH and HKrCCKrH; for these two molecules, no improvement in results was observed compared to the DFT results. Indeed, whenever the CCSD(T) calculations have converged, the results are expectedly quite similar to those from MP2, with no qualitative difference. Previous workers[10,12] had usually employed the MP2 method for organo-noble gas compounds.

Results and Discussion

Before we report results on the new molecules, it is necessary to check the accuracy of the present calculations, especially since the 3-21G limited basis set had to be adopted for molecules containing Xe. Table 1 compares the present optimized geometries of the three known linear molecules, HXeCCH, HXeCCXeH and HKrCCH, with those reported in literature[10,12]. Of the three methods employed, the RHF method expectedly predicts the shortest bond lengths due to the neglect of electron correlation (except for the Kr-C bond length). Overall, DFT/B3LYP results give the best agreement with the literature values. For the H-Ng bond lengths, the RHF values differ from the literature values by –0.12 to 0.08 Å, the MP2 values differ by 0.05 to 0.19 Å and the DFT/B3LYP values differ by 0.04 to 0.15 Å. For the Ng-C bond lengths, such differences are: RHF, –0.04 to 0.12 Å; MP2, –0.01 to 0.05 Å; DFT/B3LYP,

Table 1 — Comparison of present geometry optimizations of HXeCCH, HXeCCXeH and HKrCCH (Ng is a noble gas atom) with literature values given in parentheses. (All the molecules are linear in shape. The basis set for molecules containing xenon is 3-21G while that for the krypton molecule is DZV+**. 1 Hartree = 627.5 kcal mol^{-1}. See Table 2)

Molecule	Method	H–Ng bond length (Å)	Ng–C bond length (Å)	C–C bond length (Å)	C–H bond length (Å)	Molecular Energy (Hartree) (–*E*)	Stabilization energy (Hartree)	Correlation energy (Hartree)
HXeCCH	RHF	1.821	2.307	1.200	1.051	7276.896	- 0.368	—
	MP2	1.932	2.342	1.235	1.066	7277.136	- 0.514	- 0.240
	DFT/B3LYP	1.903	2.352	1.216	1.063	7279.951	- 0.568	- 3.055
		(1.75)[a]	(2.322)[a]	(1.225)[a]	(1.062)[a]	—	—	—
HXeCCXeH	RHF	1.861	2.273	1.210	—	14477.391	- 0.092	—
	MP2	1.970	2.361	1.251	—	14477.693	- 0.319	- 0.302
	DFT/B3LYP	1.934	2.346	1.230	—	14483.042	- 0.367	- 5.651
		(1.777)[a]	(2.314)[a]	(1.241)[a]	—	—	—	—
HKrCCH	RHF	1.470	2.365	1.212	1.060	2825.828	- 0.383	—
	MP2	1.644	2.235	1.243	1.070	2826.218	- 0.539	- 0.390
	DFT/B3LYP	1.629	2.273	1.228	1.071	2828.021	- 0.588	- 2.193
	CCSD(T)[b]	1.733	2.299	1.239	1.072	2826.261	- 0.502	- 0.433
		(1.59)[c]	(2.25)[c]	(1.24)[c]	(1.07)[c]	—	—	—

[a] MP2/LJ18/6-311G++(2d, 2p) level of theory[10].

[b] CCSD(T) geometry optimizations did not converge for the other two molecules.

[c] MP2=full/aug-cc-pVDZ level of theory[12].

0.02 to 0.03 Å. For the C-C bond lengths such differences are: RHF, 0.03 Å; MP2, 0.01 to 0.02 Å; DFT/B3LYP, 0.01 Å. For the C-H bond lengths such differences are: RHF, 0.01 Å; MP2, 0.0 to 0.01 Å; DFT/B3LYP, 0.0 Å. Thus, except for the H-Ng bond lengths for the Xe-containing molecules where a systematic increase of about 0.15 Å seems to occur in our calculations, DFT/B3LYP values for the bond lengths show excellent overall agreement with the corresponding literature values. This implies that, for the Xe-containing molecules, the H-Ng binding region[21] accumulates less electron density than it should, apparently due to the limited basis set. Note that for HKrCCH, CCSD(T) overestimates the H-Ng and Ng-C bond lengths.

Table 1 also reports the total energy, stabilization energy and correlation energy for the above three molecules. In the absence of corresponding literature values, such results are compared among themselves. The stabilization energy is obtained by subtracting the total energy of the isolated (neutral) atoms, with the same basis set (Table 2), from the molecular energy while the correlation energy is obtained by subtracting the RHF molecular energy from that obtained by MP2 or B3LYP or CCSD(T). The RHF method underestimates the stabilization energy while the MP2, CCSD(T) and DFT/B3LYP values are comparable to one another, the last showing greater stabilization. Compared to DFT/B3LYP, MP2 appears to significantly underestimate correlation energy while CCSD(T) gives slightly more correlation energy than MP2. However, it may be noted that for DFT a significant part of the interacting electronic kinetic energy is incorporated into the correlation energy, making the DFT correlation energy larger in magnitude compared to the other two methods. The total energy values decrease in the order DFT/B3LYP < CCSD(T) < MP2 < RHF. One can thus conclude that correlation energy contributes significantly to the stability and bonding of these compounds. Note that the correlation energies of Xe, Kr and Ar atoms are –2.8407, –1.7521 and –0.7011 Hartree, respectively[22].

The energetic implications of a limited basis set for atoms can be seen from Table 2 where the energies yielded by different basis sets and different methods are compared with the exact non-relativistic energies. With the 3-21G basis set, the present calculated atomic energies for Xe, Kr, C and H are above the corresponding exact non-relativistic values by less than 0.5%, 0.54%, 1.2% and 1.22%, respectively.

Table 2 — Energy values (Hartree) of neutral atom components of organo-noble gas compounds according to RHF, MP2 and DFT/B3LYP methods. (For xenon atom, the basis set is 3-21G while that for argon atom is 6–311G++ (*3d*, *3p*, *1f*). For carbon and hydrogen atoms, all the three basis sets were employed. CCSD(T) values, where different from MP2, are given in parentheses in column 3)

Atom	RHF energy (– *E*)	MP2 energy (– *E*)	DFT/B3LYP energy (– *E*)	Exact non-relativistic energy (– *E*)
Xenon	7200.7527	7200.7715 (7200.7754)	7203.2929	7235.0512[a]
Krypton				2753.8896[a]
3-21G	2739.1976	2739.2237 (2739.1976)	2740.8251	
DZV+**	2749.2489	2749.3488 (2749.3591)	2750.9348	
Argon	526.8078	526.9812 (526.9984)	527.4854	527.540[a]
Carbon				37.8450[b]
3-21G	37.3914	37.4289 (37.4559)	37.5511	
DZV+**	37.5990	37.6638 (37.7014)	37.7660	
6-311G++(3d,3p,1f)	37.6019	37.6892 (37.7284)	37.7718	
Hydrogen				0.5
3-21G	0.4962	0.4962	0.4939	
DZV+**	0.4988	0.4988	0.4983	
6-311G++(3d,3p,1f)	0.4998	0.4998	0.4989	

[a] Ref. 22.

[b] Ref. 23.

With the DZV+** basis set, such energy deficits are reduced by more than 0.36%, 0.52% and 0.52% for Kr, C and H atoms, respectively. On the other hand, with the 6-311G++ (3d, 3p, 1f) basis set, the present energies for Kr, C and H are above the corresponding exact non-relativistic energies by less than 0.14%, 0.64% and 0.22%, respectively. Since the answers to the questions on the stability and bonding of these molecules depend on energy differences rather than the absolute energies, it is quite unlikely that such departures from exact non-relativistic values for atoms would undermine our conclusions. Note that, for the non-hydrogenic atoms, DFT results are better than MP2 and CCSD(T), the latter two being close to each other.

In view of the above discussion, Table 3 presents the optimized geometries and energy values of three new, predicted molecules, HXeCCKrH, HKrCCKrH and HArCCH, all being linear in shape. While the predicted H-Ng bond lengths in HXeCCKrH appear to be overestimated by about 0.15 Å (see the Xe-containing molecules in Table 1), all other predicted bond lengths in the three molecules should be quite satisfactory. However, compared to DFT and MP2, the H-Ng and Ng-C bond lengths in HKrCCKrH appear to be overestimated by CCSD(T), just as it did in HKrCCH. The stabilization energies calculated according to the methods are comparable to those of the known molecules in Table 1, except that for HKrCCKrH CCSD(T) gives less stabilization energy compared to MP2 and DFT. Interestingly, the HArCCH molecule appears to be the most stable of the three predicted molecules although its correlation energy understandably is the least among the three molecules. A comparison with the bond lengths in the acetylene molecule (C-H, 1.060 Å; C≡C, 1.203 Å)[24] reveals that as a result of "insertion" of one Ng atom into one C-H bond of acetylene, the other C-H bond length increases up to 0.94% while the C≡C bond length increases up to 2.08%. In other words, compared to HCCH, the two carbon atoms in HNgCCH would suffer a depletion of electron density in the C-C binding region.

A more direct picture of the changes in electron density at various nuclear sites due to molecule formation from the constituent atoms, according to the DFT/B3LYP method, is given in Table 4. Even for the three known molecules, such results were not reported previously. In all the six cases, there is a pronounced increase in electron density at the proton sites with an accompanying depletion in density at the Ng and C nuclei, relative to the neutral atoms. Thus, the HXeCCH and HKrCCH molecules appear as $H^{\delta-}Ng^{\delta+}C^{\delta+}C^{\delta+}H^{\delta-}$ species, while the HXeCCXeH, HXeCCKrH and HKrCCKrH molecules appear as $H^{\delta-}Ng^{\delta+}C^{\delta+}C^{\delta+}Ng^{\delta+}H^{\delta-}$ species. However, the bonding in HArCCH is quite different from that in the other five molecules in that the former appears as $H^{\delta-}Ng^{\delta-}C^{\delta+}C^{\delta+}H^{\delta-}$ (see below). Note that in the HNgCCH molecules, the protonic site farthest away from the Ng site experiences the largest per cent increase in electron density. A topological description of the partially ionic, chage-transfer bonding in all the six molecules in terms of the electron density might

Table 3 — Optimized geometries and various energy values for the three predicted, new organo-noble gas compounds (Ng is a noble gas atom). (All the molecules are linear in shape. For the xenon-containing molecule, the basis set is 3-21G, that for the krypton-containing molecule is DZV+** and that for the argon-containing molecule is 6–311G++(*3d*, *3p*, *1f*). For HXeCCKrH, the first H–Ng value represents the H–Xe bond while the second value represents the H-Kr bond; the same sequence has been followed for the Ng-C bonds: See Table 2)

Molecule	Method	H–Ng bond length (Å)	Ng–C bond length (Å)	C–C bond length (Å)	C–H bond length (Å)	Molecular energy (Hartree) (- *E*)	Stabilization energy (Hartree)	Correlation energy (Hartree)
HXeCCKrH	RHF	1.878;1.686	2.253;2.228	1.212	—	10015.801	- 0.075	—
	MP2	1.956;1.961	2.375;2.339	1.255	—	10016.125	-0.281	- 0.324
	DFT/B3LYP	1.934;1.804	2.343;2.262	1.231	—	10020.555	- 0.348	- 4.754
HKrCCKrH	RHF	1.530	2.270	1.225	—	5574.809	- 0.116	—
	MP2	1.703	2.241	1.262	—	5575.354	- 0.327	- 0.545
	DFT/B3LYP	1.672	2.253	1.242	—	5578.755	- 0.357	- 3.946
	CCSD(T)[a]	1.827	2.339	1.255	—	5575.410	- 0.292	- 0.601
HArCCH	RHF	1.292	2.374	1.204	1.056	603.375	- 0.364	—
	MP2	1.488	2.169	1.226	1.066	603.898	- 0.538	- 0.523
	DFT/B3LYP	1.454	2.230	1.212	1.064	604.564	- 0.537	- 1.189

[a]CCSD(T) geometry optimizations did not converge for the other two molecules.

Table 4 — Electron densities (a.u.) at nuclear sites for isolated atoms and molecules, according to the DFT/B3LYP method. (The last three molecules are the predicted, new ones. The values in parentheses give the per cent density change at a nuclear site due to molecule formation. For isolated atoms, the densities were calculated by using the same basis set as that for the molecule concerned. See Table 3)

Molecule	Nuclear site	Isolated atomic density	Molecular density	Density change at nuclear site
HXeCCH	H	0.2522	0.2851	0.0329 (13.1)
	Xe	82837.75	82789.03	-48.72 (-0.06)
	C	94.899	93.811	-1.088 (-1.15)
	C	94.899	94.002	-0.897 (-0.95)
	H	0.2522	0.3593	0.1071 (42.5)
HXeCCXeH	H	0.2522	0.2829	0.0307 (12.2)
	Xe	82837.75	82788.90	-48.85 (-0.06)
	C	94.899	94.060	-0.839 (-0.88)
HKrCCH	H	0.2999	0.3345	0.0346 (11.5)
	Kr	30906.30	30877.22	-29.08 (-0.09)
	C	120.671	119.531	-1.14 (-0.94)
	C	120.671	119.377	-1.29 (-1.07)
	H	0.2999	0.4018	0.1019 (34.0)
HXeCCKrH	H	0.2522	0.4725	0.2203 (87.4)
	Xe	82837.75	72688.84	-148.91 (-0.18)
	C	94.899	78.150	-16. 749 (-17.7)
	C	94.899	78.170	-16.729 (-17.6)
	Kr	24217.31	20953.38	-3263.93 (-13.5)
	H	0.2522	0.4593	0.2071 (82.1)
HKrCCKrH	H	0.2999	0.3322	0.0323 (10.8)
	Kr	30906.30	30877.14	-29.16 (-0.09)
	C	120.671	119.646	-1.025 (-0.85)
HArCCH	H	0.2952	0.3157	0.0205 (6.94)
	Ar	3724.582	3726.758	2.176 (0.06)
	C	121.251	119.810	-1.441 (-1.19)
	C	121.251	119.951	-1.300 (-1.07)
	H	0.2952	0.4223	0.1271 (43.1)

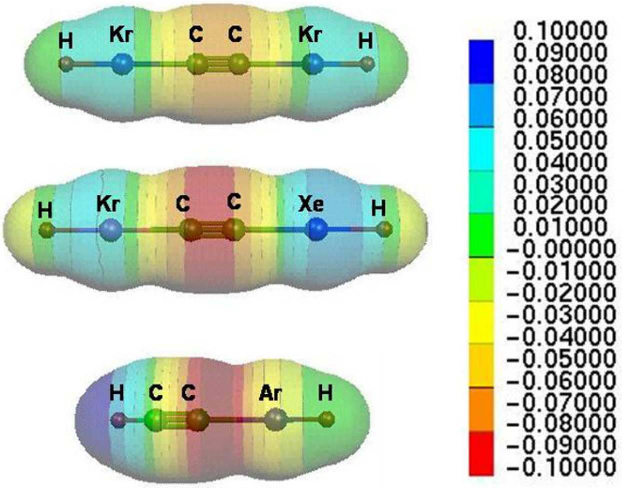

Fig. 1 — DFT/B3LYP electrostatic potential maps (a.u.) for new, predicted organo-noble gas molecules (from the top) HKrCCKrH, HKrCCXeH and HArCCH. (The accompanying colour coding shows the red and orange regions to be the most attractive regions for an electrophile).

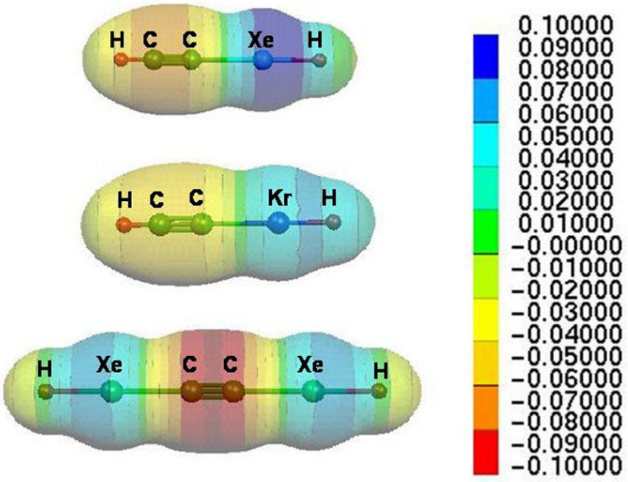

Fig. 2 — DFT/B3LYP electrostatic potential maps (a.u.) for known organo-noble gas molecules (from the top) HCCXeH, HCCKrH and HXeCCXeH. (The colour coding is the same as in Fig. 1).

be obtained via the atoms-in-molecules approach[21,25], but that has not been attempted in this paper.

Additional insights into the nature of these molecules can be obtained through their molecular electrostatic potential (ESP) maps, which are correct up to the first order in perturbation theory. The ESP is defined as[26]:

$$U(\mathbf{r}) = \Sigma_A Z_A/|\mathbf{R}_A - \int[\rho(\mathbf{r}')/|\mathbf{r}' - \mathbf{r}|]d\mathbf{r}' \qquad ...(1)$$

where ρ ($\mathbf{r}'$) is the molecular electron density at the position $\mathbf{r}'$, $\mathbf{R}_A$ is the position of nucleus A of charge Z_A and $\mathbf{r}$ is the position of an electrophile (e.g., a proton) approaching the molecule. The integration in Eq. (1) is over the entire three-dimensional space. Figure 1 shows the ESP maps of HKrCCKrH, HKrCCXeH and HArCCH while Fig. 2 depicts the ESP maps of HCCXeH, HCCKrH and HXeCCXeH molecules. The negative regions in the maps indicate the regions susceptible to electrophilic attack. Except HArCCH, all the other five molecules show the most negative regions (red/orange) to be around the carbon atoms, in particular, the C≡C bond region. For

HArCCH, the most negative region (red) has shifted from the C≡C bond to the neighbouring Ar-C bond. This again demonstrates that the bonding in HArCCH is quite different (see above) from that in the other five molecules.

Finally, answers to the questions about the stability of the organo-noble gas compounds can not be complete without examining their possible dissociation channels. Apart from dissociating into neutral atoms, the three possible dissociation channels are those which yield the following dissociation products: *Channel A*, HCCH + Ng1 and/or Ng2; *Channel B*, H + Ng1 and/or Ng2 + CCH; *Channel C*, 2 H + Ng1 and/or Ng2 + CC.

Table 5 reports the energies of HCCH, CCH and CC according to different basis sets and methods. Comparing with the neutral-atom energies in Table 2, all these three species are stable. The dissociation energies of all the six molecules according to the channels A, B and C are presented in Table 6 (the CCSD(T) results are comparable to those from MP2). All the molecules are unstable according to channel A, showing negative dissociation energies. Therefore, these molecules cannot be prepared by inserting noble gas atoms into the acetylene molecule. Of the three known molecules, HXeCCH and HKrCCH are stable (positive dissociation energy) according to channel B using MP2 as well as DFT/B3LYP, but unstable using the RHF, reinforcing our conclusion above on the significance of electron correlation in the bonding of those molecules. It is rather interesting that, for all the six molecules, channel C gives the energetically most favourable dissociation pathway. However, only DFT/B3LYP gives stability according to channel C for the three molecules containing the two noble gas atoms, the new molecule HXeCCKrH being the least stable, with a dissociation energy of 19.6 kcal mol^{-1}; the corresponding dissociation energies of the known molecule HXeCCXeH and the new molecule HKrCCKrH are 31.7 and 26.5 kcal mol^{-1}, respectively. For the stable series HNgCCH, the dissociation energies according to channel C decrease in the order Xe > Kr > Ar, with the Ar-containing molecule's dissociation energy being 136.5 kcal mol^{-1}, according to DFT/B3LYP. Therefore, HArCCH is unstable according to channel B (see also ref. 15) but

Table 5 — Energy values (Hartree) in optimized geometries for possible neutral, non-atomic dissociation fragments of organo-noble gas compounds (see Table 2 for neutral atomic fragments) according to RHF, MP2 and DFT/B3LYP methods as well as three different basis sets. (CCSD(T) values for only the DZV+** basis set are given within parentheses in column 3)

Fragment basis sets	RHF energy ($-E$)	MP2 energy ($-E$)	DFT/B3LYP energy ($-E$)
HCCH			
3-21G	76.3960	76.5793	76.8560
DZV+**	76.8326	77.0863 (77.1130)	77.2863
6-311G++(3d, 3p, 1f)	76.8497	77.1603	77.3124
CCH			
3-21G	75.7320	75.8628	76.1390
DZV+**	76.1623	76.3554 (76.4011)	76.5543
6-311G++(3d, 3p, 1f)	76.1765	76.4226	76.5901
CC			
3-21G	74.9543	75.2209	75.4179
DZV+**	75.3896	75.7021 (75.7282)	75.8466
6-311G++(3d ,3p, 1f)	75.4001	75.7606	75.8633

Table 6 — Dissociation energies (Hartree) of the organo-noble gas compounds, with reference to possible dissociation channels (except dissociation into neutral atoms; see Tables 1 and 3). (The last three molecules are the new, predicted ones. The basis sets are as specified in Table 2. Ng1/Ng2 is a noble gas atom. The dissociation products are: Channel A, HCCH + Ng1 and/or Ng2; Channel B, H + Ng1 and/or Ng2 + CCH; Channel C, 2 H + Ng1 and/or Ng2 + CC. See Table 5. CCSD(T) values for only two molecules, where geometry optimizations have converged, are given in parentheses in column 4)

Molecule	Dissociation channel	Dissociation energy RHF	MP2	DFT/B3LYP
	A	-0.2527	-0.2148	-0.1979
HXeCCH	B	-0.0849	0.0055	0.0252
	C	0.1966	0.1512	0.2524
	A	-0.5104	-0.4293	-0.3998
HXeCCXeH	B	-0.3426	-0.2090	-0.1767
	C	-0.0611	-0.0633	0.0505
	A	-0.2535	-0.2171(-0.2111)	-0.2001
HKrCCH	B	-0.0820	0.0150(0.0020)	0.0336
	C	0.1919	0.1695(0.1761)	0.2430
	A	-0.5453	-0.4495	-0.4190
HXeCCKrH	B	-0.3775	-0.2292	-0.1959
	C	-0.0960	-0.0835	0.0313
	A	-0.5214	-0.4299(-0.4212)	-0.4009
HKrCCKrH	B	-0.3499	-0.1978(-0.2081)	-0.1672
	C	-0.0760	-0.0433(-0.0340)	0.0422
	A	-0.2825	-0.2435	-0.2338
HArCCH	B	-0.1091	-0.0056	-0.0104
	C	0.1675	0.1566	0.2175

stable according to channel C. Therefore, all the new, predicted molecules should be amenable to synthesis under conditions which can generate the C_2 species.

Now, considering the internuclear axis of HCCH as a direction of reference for molecules containing two noble gas atoms, one may examine the preferred stereochemical approach of two noble gas atoms to the acetylene molecule. Taking HXeCCXeH as a representative example, we examined two possible modes: Planar, *cis* and *trans*; non-planar, with dihedral angles 50°, 90° and 120°. Of both these modes, the non-planar approach of two Xe atoms with 90° dihedral angle is energetically more favourable. We have also tried to insert a Kr atom laterally between two benzene molecules as well as into the C-C bond between the rings in biphenyl molecule. These were energetically unfavourable. The same is true if one tries to insert a Xe atom as a sandwich between two benzene molecules. It may be noted that all the calculations reported in this paper satisfy the quantum mechanical virial theorem, $-\langle V \rangle / \langle T \rangle = 2$, within the error range 0.0095% to 0.25%.

Conclusions

The three new, predicted, linear organo-noble gas molecules HKrCCKrH, HKrCCXeH and HArCCH, incorporating both one and two noble gas atoms into the acetylene framework, are all stable according to the present calculations. Conclusions on their optimized geometry, stability, nature of bonding, dissociation channel and propensity to attack by electrophiles have been reached by a careful comparison with similar results for the known molecules HXeCCH, HKrCCH and HXeCCXeH. It was observed that the present predicted molecules fall into the same qualitative patterns as those of the known molecules, leading to the conclusion that the new molecules should also be capable of independent existence. Apart from dissociation into neutral atoms, the most favourable dissociation channel for all the six molecules yields the C_2 species as a dissociation product. Therefore, such organo-noble gas compounds could be synthesized under conditions which generate the C_2 species. Except HArCCH, the bonding in the other five molecules is partially ionic for the H-Ng and C-H bonds. For HArCCH, the bonding is different from that in the other molecules, being partially ionic for the Ng-C and C-H bonds. The correlation energy plays a significant role in the bonding of these partially ionic, charge-transfer molecules. However, a noble gas atom could not be incorporated into the biphenyl molecule between the phenyl rings as well as between two benzene molecules in both lateral and sandwich modes. For molecules containing two noble gas atoms, a non-planar mode of approach with the two noble gas atoms forming a 90° dihedral angle with the HCCH internuclear axis is energetically and therefore stereochemically the most favourable. The conclusions reached in this paper should be independent of the methods and the basis sets employed.

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References

1 Lundell J, Khriachtchev L, Pettersson M & Räsänen M, *Low Temp Phys*, 26 (2000) 680.
2 Khriachtchev L, Pettersson M, Runeberg N, Lundell J & Räsänen M, *Nature*, 406 (2000) 874.
3 Khriachtchev L, Pettersson M, Lignell A & Räsänen M, *J Am Chem Soc*, 123 (2001) 8610.
4 Lundell J, Chaban G M &Gerber R B, *J Phys Chem A*, 104 (2000) 7944.
5 McDowell S A C, *Phys Chem Chem Phys*, 5 (2003) 1530.
6 Lundell J, Khriachtchev L, Pettersson M & Räsänen M, *Phys Chem Chem Phys,* 5 (2003) 3334.
7 Pettersson M, Lundell J, Khriachtchev L, Isiniemi E & Räsänen M, *J Am Chem Soc*, 120 (1998) 7979.
8 Pettersson M, Lundell J, Khriachtchev L & Räsänen M, *J Chem Phys*, 109 (1998) 618.
9 Berski S, Latajka Z, Silvi B & Lundell J, *J Chem Phys*, 114 (2001) 4349.
10 Lundell J, Cohen A & Gerber R B, *J Phys Chem*, *A* 106 (2002) 11950.
11 Khriachtchev L, Tanskanen H, Lundell J, Pettersson M, Kiljunen H & Räsänen M, *J Am Chem Soc*, 125 (2003) 4696.
12 Khriachtchev L, Tanskanen H, Cohen A, Gerber R B, Lundell J, Pettersson M, Kiljunen H & Räsänen M, *J Am Chem Soc*, 125 (2003) 6876.
13 Christie K O, *Angew Chem Int Edn*, 40 (2001) 1419.
14 Gerber R B, *Annu Rev Phys Chem*, 55 (2004) 55.
15 Sheng Li, Cohen A & Gerber R B, *J Am Chem Soc*, 128 (2006) 7156.
16 Sheng Li & Gerber R B, *J Chem Phys*, 124 (2006) 231103.
17 Maggiarosa N, Naumann D & Tyrra W, *Angew Chem Int Ed*, 39 (2000) 4588.

18 Schmidt M W, Baldridge K K, Boatz J A, Elbert S T, Gordon M S, Jensen J H, Koseki S, Matsunaga N, Nguyen K A, Su S J, Windus T L, Dupuis M & Montgomery J A, *GAMESS: General Atomic and Molecular Electronic Structure System*, *J Comp Chem*, 14 (1993) 1347. See other references therein. Grateful acknowledgement is made for permission to use GAMESS.

19 Schaftenaar G & Noordik J H, *J Comp-Aided Mol Design,* 14 (2000) 123.

20 Portmann S & Luthi H P, *MOLEKEL: An Interactive Molecular Graphics Tool*, *Chimia,* 54 (2000) 766.

21 Bader R F W, in *The Force Concept in Chemistry*, edited by B M Deb (Van Nostrand-Reinhold, New York) 1981.

22 Roy A K, Dey B K & Deb B M, *Chem Phys Lett*, 308 (1999) 523.

23 Davidson E R, Hagstrom S A, Chakravorty S J, Umar V M & Fischer C F, *Phys Rev A*, 44 (1991) 7071.

24 *CRC Handbook of Chemistry and Physics*, edited by D R Lide, 85th Edn (CRC Press, New York) 2004, Table 9-26.

25 Bader R F W, *Atoms in Molecules* (Clarendon Press, Oxford) 1990.

26 Bonaccorsi R, Scrocco E & Tomasi J, *J Chem Phys*, 52 (1970) 5270.