Supplementary material

Tailoring the electronic properties among oxoarsine, arsinoyl and arsine oxide isomers: the simplest molecular systems with an arsenic-oxygen bond

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Table S1. Relative energy gap (in kcal mol^{-1}) among the HAsO isomers

Method	i1	i2	i3	i4
CCSD(T)/CBS	0.0	37.4	18.0	1.2
QCISD(T,Full)/aug-cc-pVQZ	0.0	37.4	19.8	2.8
G4*	0.0	39.8	16.8	2.3
G4MP2*	0.0	40.2	17.1	2.4
G4	0.0	37.5	14.6	-2.2
G4MP2	0.0	39.8	14.8	-2.2

Table S2. The zero-point vibrational energy (ZPVE, in kcal mol^{-1}) obtained with three different methodologies among the AsOH$_n$ isomers (n=0-3)

Radical	QCISD	G4	$\Delta_{ZPVE(QCISD-G4)}$	B3LYP/cc-pVTZ	$\Delta_{ZPVE(QCISD-B3LYP)}$
AsO	1.42	1.42	0.00	1.44	-0.02
i1	5.62	7.6	-1.97	5.40	0.23
i2	4.97	4.69	0.28	4.68	0.28
i3	8.05	7.78	0.27	7.86	0.19
i4	7.89	5.36	2.53	7.68	0.21
i5	12.81	12.33	0.48	12.43	0.38
i6	13.08	12.59	0.49	12.70	0.37
i7	10.98	14.95	-3.97	10.47	0.51
i8	15.41	10.37	5.04	18.02	-2.61
i9	17.75	18.01	-0.26	16.88	0.88
i10	18.83	17.96	0.87	18.13	0.7
i11	18.83	16.65	2.17	18.08	0.74
i12	20.11	19.45	0.66	19.59	0.52
i13	20.11	19.4	0.71	19.56	0.55

Table S3. Calculated and experimental vibrational frequencies (in cm^{-1}) of HAsO (**i1**), as well as the mean unassigned error (MUE) and mean absolute error (MAE) in to the prediction of the frequencies

Method	ν_1	ν_2	ν_3	reference	MUE	MAE
QCISD/cc-pVTZ	881.2	988.2	2064.5	This study	78	37
B3LYP/cc-pVTZ	853.2	979.7	1942.4	This study	25	12
G4	728.0	1011.5	3783.1	This study	607	830
B3LYP/aug-cc-pV5Z	849	974	1970	[53]	31	10
CCSD(T)/aug-cc-pV5Z	864	961	2027	[53]	51	30
Experimental	**832.4**	**937.0**	**1931.0**	[53]		

Table S4. Calculated and experimental vibrational frequencies (in cm^{-1}) of H_2AsO (**i7**), as well as the mean unassigned error (MUE) and mean absolute error (MAE) in to the prediction of the frequencies

Method	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	Reference	MUE	MAE
QCISD/cc-pVTZ	535.33	746.85	867.11	1010.01	2244.31	2275.3	This study	81	70
B3LYP/cc-pVTZ	546.39	720.72	843.5	980.62	2098.68	2135.03	This study	34	21
G4	547.74	719.79	843.56	981.98	2115.83	2151.83	This study	39	27
B3LYP/6-311G(d,p)	519	717	806	994	2100	2137	[51]	22	41
QCISD/6-311G(d,p)	497	741	807	1032	2203	2224	[51]	51	82
CCSD(T)/6-311G(d,p)	454	733	812	1021	2178	2204	[51]	33	82
CCSD/6-311G(d,p)	451	754	808	1039	2214	2234	[51]	45	97
B3LYP/6-311++G(3df,3pd)	538	716	843	978	2105	2144	[51]	33	25
QCISD/6-311++G(3df,3pd)	520	735	859	994	2203	2229	[51]	61	60
CCSD(T)/6-311++G(3df,3pd)	507	712	875	973	2174	2206	[51]	49	51
CCSD/6-311++G(3df,3pd)	499	743	880	1003	2239	2267	[51]	72	72
B3LYP/aug-cc-pVTZ	541	717	841	975	2105	2144	[51]	33	26
QCISD/aug-cc-pVTZ	524	738	863	1003	2235	2272	[51]	73	70
CCSD(T)/aug-cc-pVTZ	515	705	878	981	2204	2244	[51]	61	60
CCSD/aug-cc-pVTZ	485	750	883	1014	2260	2302	[51]	77	80
Experimental	525.7		838.7	946.1	2022.9		[52]		

Table S5. Energetic profile (in kcal mol^{-1}) among the H_2AsO isomers

Reaction	CCSD(T)/CBS	ROCCSD(T)/aug-cc-pVQZ	UCCSD(T)/aug-cc-pVQZ
i5	0.5	0.5	0.5
TS4	3.1	3.1	3.1
i6	0.0	0.0	0.0
TS3	53.7	53.8	53.9
i7	28.8	29.3	29.2
TS5	58.4	57.8	57.9
i8	47.5	46.8	46.8
TS6	55.9	56.4	56.3
AsO+H_2	27.4	26.5	27.1

Table S6. Relative energy gap (in kcal mol^{-1}) among the H_2AsO isomers

Method	i6	i5	i7	i8
CCSD(T)/CBS	0.0	0.5	28.8	47.5
ROCCSD(T)/aug-cc-pVQZ	0.0	0.5	29.3	46.8
UCCSD(T)/aug-cc-pVQZ	0.0	0.5	29.2	46.8
G4*	0.0	0.4	28.2	47.0
G4MP2*	0.0	0.4	28.5	48.0
G4	0.0	0.4	32.7	42.4
G4MP2	0.0	0.4	32.9	43.4

Table S7. Arsenic [q(As)] and oxygen [q(O)] partial atomic charge by different population methodologies

Molecule	NPA		QTAIM		CHELP		CHELPG		MK		CM5	
	q(As)	q(O)	q(As)	q(O)	q(As)	q(O)	q(As)	q(O)	q(As)	q(O)	q(As)	q(O)
AsO	0.88	-0.88	0.95	-0.95	0.36	-0.36	0.35	-0.35	0.34	-0.34	0.30	-0.30
i1	1.07	-0.89	1.32	-0.98	0.41	-0.37	0.40	-0.38	0.38	-0.37	0.38	-0.32
i2	0.61	-0.57	0.90	-0.70	0.20	-0.24	0.16	-0.23	0.14	-0.22	0.18	-0.19
i3	0.44	-0.93	0.52	-1.10	0.10	-0.29	0.04	-0.35	0.03	-0.36	0.07	-0.24
i4	0.51	-0.99	0.56	-1.14	0.15	-0.41	0.10	-0.43	0.09	-0.44	0.12	-0.28
i5	0.62	-0.95	0.88	-1.14	0.21	-0.49	0.12	-0.45	0.10	-0.46	0.17	-0.28
i6	0.58	-0.94	0.86	-1.13	0.19	-0.30	0.04	-0.49	0.02	-0.51	0.15	-0.27
i7	0.89	-0.74	1.39	-0.87	0.29	-0.35	0.26	-0.34	0.22	-0.32	0.30	-0.29
i8	-0.16	-0.86	-0.10	-1.15	-0.30	-0.11	-0.28	-0.42	-0.29	-0.46	-0.27	-0.13
i9	1.26	-1.02	1.94	-1.11	0.96	-0.66	0.79	-0.60	0.62	-0.56	0.43	-0.43
i10	0.66	-0.96	1.19	-1.15	0.30	-0.52	0.04	-0.49	-0.01	-0.52	0.21	-0.30
i11	0.71	-0.97	1.23	-1.16	0.18	-0.46	0.16	-0.48	0.13	-0.48	0.23	-0.30
i12	-0.09	-0.84	0.21	-1.15	-0.23	-0.17	-0.32	-0.54	-0.35	-0.58	-0.21	-0.13
i13	-0.06	-0.84	0.23	-1.15	-0.25	-0.16	-0.25	-0.43	-0.27	-0.47	-0.19	-0.13

Table S8. Linear correlation between the ν(As-O) frequencies and δq [q(As)-q(O)] using the vibrational frequencies calculated with QCISD/cc-pVTZ and B3LYP/cc-pVTZ

Method	QCISD	B3LYP
NPA	0.832	0.795
QTAIM	0.531	0.483
CHELP	0.692	0.648
CHELPG	0.618	0.600
MK	0.662	0.642
CM5	0.896	0.855

Table S9. Bond order analysis with bond delocalization index (bo_{bdi}), natural resonance theory bond index (bo_{nrt}), Mayer bond index (bo_{mayer}), Wiberg bond index (bo_{wi}), atom-atom overlap natural atomic orbital bond index (bo_{nao}), and atomatom overlap natural localized molecular orbitals/natural population analysis bond index (bo_{nlmo})

Molecule	bo_{wi}	bo_{bdi}	bo_{mayer}	bo_{nrt}	bo_{nao}	bo_{nlmo}
AsO	1.59	1.76	2.03	1.50	0.99	1.12
i1	1.63	1.75	2.08	2.03	0.93	1.08
i2	1.03	1.09	1.26	1.82	0.74	0.86
i3	0.97	1.30	1.25	2.00	0.66	0.57
i4	0.74	1.02	1.20	1.52	0.61	0.5
i5	0.76	0.94	1.01	1.49	0.59	0.52
i6	0.77	0.97	1.02	1.50	0.59	0.53
i7	1.15	1.16	1.52	1.50	0.88	1.24
i8	0.31	0.63	0.39	1.00	0.27	0.17
i9	1.21	1.31	1.86	1.13	1.21	0.82
i10	0.77	0.93	1.04	1.02	0.58	0.49
i11	0.76	0.90	1.02	1.01	0.58	0.48
i12	0.34	0.58	0.40	1.00	0.28	0.18
i13	0.34	0.94	0.39	1.00	0.28	0.18

Table S10. Linear correlation between the ν(As-O) frequencies and As-O bond order indexes using the vibrational frequencies calculated with QCISD/cc-pVTZ and B3LYP/cc-pVTZ

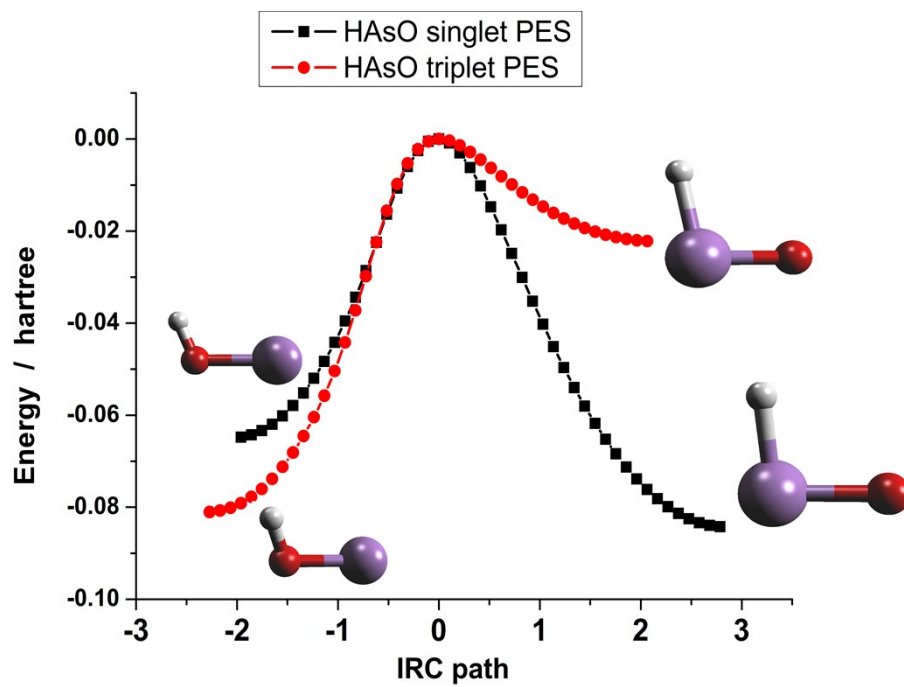| Method	QCISD	B3LYP
bo_{wi}	0.88	0.92
bo_{bdi}	0.68	0.74
bo_{mayer}	0.94	0.97
bo_{nrt}	0.28	0.28
bo_{nao}	0.9	0.91
bo_{nlmo}	0.77	0.81

Figure S1. The HAsO singlet and triplet potential energy surfaces obtained by IRC calculations

HAsO (i1)
Charge = 0 Multiplicity = 1
 As,0,-0.0000045462,0.,0.0099762376
 H,0,0.0047569384,0.,1.5595289234
 O,0,1.5917954707,0.,-0.3324163068

HAsO (i2)
Charge = 0 Multiplicity = 3
 As,0,0.0017654856,0.,0.0100144732
 H,0,0.0015720984,0.,1.5293449005
 O,0,1.7260067256,0.,-0.1131522037

AsOH (i3)
Charge = 0 Multiplicity = 1
 As,0,0.0057652286,0.,0.0135137781
 O,0,-0.0030148675,0.,1.7748725332
 H,0,0.9016779412,0.,2.0994947547

AsOH (i4)
Charge = 0 Multiplicity = 3
 As,0,0.0075583598,0.,0.0158967372
 O,0,-0.0050710254,0.,1.796593505
 H,0,0.888626577,0.,2.1475483211

cis-HAsOH (i5)
Charge = 0 Multiplicity = 2
 O,0,0.0085349568,0.,-0.001854195
 H,0,0.0197651601,0.,0.9563838445
 As,0,1.6645542046,0.,-0.6658984035
 H,0,2.3966424818,0.,0.6698477101

trans-HAsOH (i6)
Charge = 0 Multiplicity = 2
 O,0,0.0037431526,0.,-0.0070136442
 H,0,0.0122314714,0.,0.9527251952
 As,0,1.6947643332,0.,-0.5863897692
 H,0,1.2612699153,0.,-2.0361776939

H$_2$AsO (i7)
Charge = 0 Multiplicity = 2
 As,0,0.0078297497,0.0025357286,0.0066481335
 H,0,0.0025625199,0.0016311143,1.5153026995
 H,0,1.4956647764,0.0016311142,-0.243178359
 O,0,-0.5720119592,1.4990509633,-0.4856875444

AsOH$_2$ (i8)
Charge = 0 Multiplicity = 2
 O,0,0.0007625715,0.002991846,-0.002070777
 H,0,-0.0012883083,-0.0051807424,0.9580972878
 As,0,2.0367855924,-0.0006914342,-0.6939020206
 H,0,-0.4289342617,-0.8033543874,-0.2972996581

H$_3$AsO (i9)
Charge = 0 Multiplicity = 1
 As,0,0.0027463138,-0.0035704209,0.0022326112
 H,0,0.0008302844,-0.0010794341,1.5023816713
 H,0,1.4709019074,-0.0010794341,-0.3059394618
 H,0,-0.3763332246,-1.4219447565,-0.3059394618
 O,0,-0.8847886144,1.1502938295,-0.7192874156

trans-H$_2$AsOH (i10)
Charge = 0 Multiplicity = 1
 As,0,0.0059179462,0.0142654137,0.0057964852
 H,0,-0.0055554816,0.005768046,1.5176208564
 H,0,1.5171818571,0.0057683766,-0.0369371674
 O,0,-0.1895090286,1.7856424577,-0.1856289278
 H,0,-0.8658495925,1.9306632458,-0.8481289229

cis-H$_2$AsOH (i11)
Charge = 0 Multiplicity = 1
 As,0,0.0080455474,0.0102366288,0.0079751325
 H,0,-0.0035327368,0.0121397871,1.5261731125
 H,0,1.5260825937,0.012139291,-0.0169779695
 O,0,-0.2814601854,1.7484861434,-0.2789918003
 H,0,0.279491381,2.2907183269,0.2770376719

trans-HAsOH$_2$ (i12)
Charge = 0 Multiplicity = 1
 As,0,0.0000547496,-0.0000888037,0.0035094897
 O,0,-0.0031400954,0.0050338441,2.1460730568
 H,0,0.9098252013,0.0016345158,2.4445473747
 H,0,-0.4017854838,-0.8163060153,2.4445471789
 H,0,-0.798591697,1.2805819815,0.087799336

cis-HAsOH$_2$ (i13)
Charge = 0 Multiplicity = 1
 As,0,0.0051914365,-0.0000048607,0.0034367311
 H,0,0.0259802675,0.0000064292,1.5231707609
 O,0,2.140327308,0.0000012506,0.0971261397
 H,0,2.4250155092,-0.7731079562,0.5910565444
 H,0,2.4250108602,0.7731140823,0.591053542

TS1
Charge = 0 Multiplicity = 1
 As,0,0.0066094458,0.,-0.0006522718
 O,0,0.0045907552,0.,1.7616531549
 H,0,1.1682568582,0.,1.0706096719

TS2
Charge = 0 Multiplicity = 3
 As,0,0.0104966412,0.,0.0101824566
 O,0,-0.0024553593,0.,1.7682569622
 H,0,1.2499892501,0.,1.0021929019

TS3
Charge = 0 Multiplicity = 2
 O,0,0.0066150191,-0.0029632787,0.009042428
 As,0,0.0084646311,-0.0091157097,1.7853056836
 H,0,1.5158846705,0.0015338355,2.0314442577
 H,0,-0.0265669897,-1.2373243468,0.7796590656

TS4
Charge = 0 Multiplicity = 2
 O,0,0.0043571425,-0.0035786568,-0.0075988618
 H,0,0.017568027,-0.006913802,0.9512371918
 As,0,1.6647134786,-0.0049554889,-0.6703483045
 H,0,1.8053638607,-1.5177284488,-0.8114113375

TS5
Charge = 0 Multiplicity = 2
 O,0,-0.0081169363,0.0034013799,-0.0066502603
 H,0,0.0170101964,-0.0071228129,0.9579625114
 As,0,1.9720015926,-0.0069508439,-0.5955390842
 H,0,0.6572474716,-0.9909433775,-0.4233301166

TS6
Charge = 0 Multiplicity = 2
 As,0,-0.0009634917,-0.0002507844,-0.0023092117
 H,0,0.0388944319,-0.0030123802,1.6355042711
 H,0,1.1350652421,-0.0030124058,1.178140014
 O,0,-0.0926428438,-1.662253478,-0.2220382038
TS7
Charge = 0 Multiplicity = 1
 As,0,0.0066775684,0.011255398,0.0063731429
 H,0,-0.002341021,0.0058425709,1.5210236359
 H,0,1.5263268892,0.0144500193,-0.0148788572
 O,0,-0.2604303653,1.7797657296,-0.1647448401
 H,0,0.4136745764,2.1608191111,-0.7281160386

TS8
Charge = 0 Multiplicity = 1
 As,0,-0.0003735422,0.003703995,0.0180067085
 O,0,-0.009793204,-0.0011401704,2.0784035478
 H,0,0.9238594542,0.0033008186,2.3199102892
 H,0,-1.4689594093,-0.3390165901,0.0507612888
 H,0,-0.1501094521,1.0045790787,1.3152394932

TS9
Charge = 0 Multiplicity = 1
 As,0,0.005518864,0.0100831698,0.0045813007
 H,0,0.0009124477,-0.0048468809,1.5105881455
 H,0,1.4849423783,-0.0048469864,-0.2771702167
 H,0,-1.1588680057,0.1831387045,-0.9619838951
 O,0,-0.8296001932,-1.3291110331,-0.6886564367

TS10
Charge = 0 Multiplicity = 1
 As,0,-0.0000928277,-0.0032831918,-0.0049715555
 O,0,-0.0000761969,-0.0028022037,2.1085182242
 H,0,0.7875709568,-0.0047497011,2.6500894659
 H,0,-0.7866822921,0.0376878635,2.6500924466
 H,0,-0.0408803282,-1.5161888832,0.063015776

TS11
Charge = 0 Multiplicity = 1
 As,0,0.0073161452,0.0120178103,0.0043249967
 O,0,0.0024164308,0.0032551081,1.7016318599
 H,0,1.5011741099,0.0148448373,-0.3709956718
 H,0,0.3182857555,1.3177290457,1.0755057992
 H,0,0.3630112701,1.7871061032,0.2530219038

TS12
Charge = 0 Multiplicity = 1
 As,0,0.0011123666,0.0030820137,0.0024899176
 H,0,0.0012644501,-0.0054551893,1.5097835406
 H,0,1.5117722553,-0.0198692028,-0.2629822475
 H,0,1.309426214,-0.9950141349,0.5788700681
 O,0,-1.0642610802,-0.9467520163,-0.7852076427

TS13
Charge = 0 Multiplicity = 1
As
 O,1,B1
 H,1,B2,2,A1
 H,2,B3,1,A2,3,D1,0
 H,1,B4,2,A3,4,D2,0
    Variables:
 B1=1.71011221
 B2=1.56652061
 B3=1.49821411
 B4=1.86438785
 A1=104.18370376
 A2=65.211218
 A3=82.1302687
 D1=76.66567853
 D2=-2.10201119

TS14
Charge = 0 Multiplicity = 1
As
 H,1,B1
 H,1,B2,2,A1
 H,1,B3,2,A2,3,D1,0
 O,1,B4,2,A3,4,D2,0
    Variables:
 B1=1.52605045
 B2=1.54737182
 B3=1.76197489
 B4=1.63886162
 A1=100.54755909
 A2=70.22446342
 A3=119.05804965
 D1=37.74183371
 D2=100.76629796