Development and implementation of advanced fitting methods for the calculation of accurate molecular structures

Supporting Information

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Tables S1, S2 and S3 report the definitions of A_1-WDICs of diacetylene, ketene and benzene in terms of redundant internal coordinates. These coordinates have been employed to obtain the semi-experimental equilibrium geometries of the three compounds.

Tables S4, S5 and S6 describe the structures of Z-matrices employed to derive the semi-experimental equilibrium structures of diacetylene, ketene and benzene.

Table S7 reports the values of predicate observations and assigned uncertainties used for fluorohydroxyborane, methenammine and nitric acid. This set of values has been taken from Refs.[1–3]

Table S8 reports the theoretical equilibrium geometry of the Ip conformer of glycine computed at both B2PLYP/VTZ and B3LYP/SNSD levels.

Table S1: Definition of A_1-WDICs of diacetylene in terms of redundant internal coordinates.

Red. int. coord.[a]	A_1-WDICs[b]		
	s_1	s_2	s_3
BL (H1−C1)	0.3188	0.5974	0.2037
BL (C1−C2)	0.5136	−0.1128	−0.4728
BL (C2−C3)	0.5189	−0.5107	0.6855
BL (C3−C4)	0.5136	−0.1128	−0.4728
BL (C4−H2)	0.3188	0.5974	0.2037
BA (H1−C2−C3)	0.0000	0.0000	0.0000
BA (C3−C2−H1)	0.0000	0.0000	0.0000
BA (C1−C2−C3)	0.0000	0.0000	0.0000
BA (C3−C2−C1)	0.0000	0.0000	0.0000
BA (C2−C3−C4)	0.0000	0.0000	0.0000
BA (C4−C3−C2)	0.0000	0.0000	0.0000
BA (C3−C4−H2)	0.0000	0.0000	0.0000
BA (H2−C4−C3)	0.0000	0.0000	0.0000

a) Redundant internal coordinates in terms of atomic centers; BL: bond length, BA: bond angle. See Figure 2a of main text for atom numbering.
b) Linear combination coefficients appearing in definitions of non-redundant internal coordinates.

Table S2: Definition of A_1-WDICs of ketene in terms of redundant internal coordinates.

Red. int. coord.[a]	A_1-WDICs[b]			
	s_1	s_2	s_3	s_4
BL (C2−O)	0.3649	−0.2054	−0.6912	−0.5890
BL (C1−C2)	0.6192	−0.2921	−0.1867	0.7046
BL (C2−H1)	0.0245	−0.5934	0.3404	−0.1773
BL (C2−H2)	0.0245	−0.5934	0.3404	−0.1773
BA (C1−C2−H1)	0.3027	0.1788	0.2204	−0.1335
BA (C1−C2−H2)	0.3027	0.1788	0.2204	−0.1335
BA (H1−C2−H1)	−0.5468	−0.3230	−0.3981	0.2412
BA (O−C1−C2)	0.0000	0.0000	0.0000	0.0000
BA (C2−C1−O)	0.0000	0.0000	0.0000	0.0000
OOP (C2−H1−H2−C1)	0.0000	0.0000	0.0000	0.0000

a) Redundant internal coordinates in terms of atomic centers; BL: bond length, BA: bond angle, OOP: out-of-plane. See Figure 2b of main text for atom numbering.
b) Linear combination coefficients appearing in definitions of non-redundant internal coordinates.

Table S3: Definition of A_1-WDICs of benzene in terms of redundant internal coordinates.

Red. int. coord.[a]	A_1-WDICs[b]	
	s_1	s_2
BD (C1−H1)	0.2277	−0.3388
BD (C2−H2)	0.2277	−0.3388
BD (C3−H3)	0.2277	−0.3388
BD (C4−H4)	0.2277	−0.3388
BD (C5−H5)	0.2277	−0.3388
BD (C6−H6)	0.2277	−0.3388
BD (C1−C2)	0.3388	0.2277
BD (C2−C3)	0.3388	0.2277
BD (C3−C4)	0.3388	0.2277
BD (C4−C5)	0.3388	0.2277
BD (C5−C6)	0.3388	0.2277
BD (C1−C6)	0.3388	0.2277
BA (C2−C1−C6)	0.0000	0.0000
BA (C2−C1−H1)	0.0000	0.0000
BA (C6−C1−H1)	0.0000	0.0000
BA (C3−C2−C1)	0.0000	0.0000
BA (C1−C2−H2)	0.0000	0.0000
BA (C3−C2−H2)	0.0000	0.0000
BA (C4−C3−C2)	0.0000	0.0000
BA (C2−C3−H3)	0.0000	0.0000
BA (C4−C3−H3)	0.0000	0.0000
BA (C5−C4−C3)	0.0000	0.0000
BA (C3−C4−H4)	0.0000	0.0000
BA (C5−C4−H4)	0.0000	0.0000
BA (C6−C5−C4)	0.0000	0.0000
BA (C4−C5−H5)	0.0000	0.0000
BA (C6−C5−H5)	0.0000	0.0000
BA (C1−C6−C5)	0.0000	0.0000
BA (C1−C6−H6)	0.0000	0.0000
BA (C5−C6−H6)	0.0000	0.0000
DA (C3−C2−C1−C6)	0.0000	0.0000
DA (C3−C2−C1−H1)	0.0000	0.0000
DA (H2−C2−C1−H1)	0.0000	0.0000
DA (C5−C6−C1−H1)	0.0000	0.0000
DA (H6−C6−C1−H1)	0.0000	0.0000
DA (C6−C1−C2−H2)	0.0000	0.0000
DA (C4−C3−C2−H2)	0.0000	0.0000
DA (C4−C3−C2−C1)	0.0000	0.0000
DA (C1−C2−C3−H3)	0.0000	0.0000
DA (H2−C2−C3−H3)	0.0000	0.0000
DA (C5−C4−C3−H3)	0.0000	0.0000
DA (C5−C4−C3−C2)	0.0000	0.0000
DA (C2−C3−C4−H4)	0.0000	0.0000
DA (H3−C3−C4−H4)	0.0000	0.0000

DA (C6−C5−C4−H4)	0.0000	0.0000
DA (C6−C5−C4−C3)	0.0000	0.0000
DA (C3−C4−C5−H5)	0.0000	0.0000
DA (H4−C4−C5−H5)	0.0000	0.0000
DA (C1−C6−C5−C4)	0.0000	0.0000
DA (C1−C6−C5−H5)	0.0000	0.0000
DA (C2−C1−C6−C5)	0.0000	0.0000
DA (C2−C1−C6−H6)	0.0000	0.0000
DA (C4−C5−C6−H6)	0.0000	0.0000
DA (H5−C5−C6−H6)	0.0000	0.0000
OOP (C1−C2−C6−H1)	0.0000	0.0000
OOP (C2−C1−C3−H2)	0.0000	0.0000
OOP (C3−C2−C4−H3)	0.0000	0.0000
OOP (C4−C3−C5−H4)	0.0000	0.0000
OOP (C5−C4−C6−H5)	0.0000	0.0000
OOP (C6−C1−C5−H6)	0.0000	0.0000

a) Redundant internal coordinates in terms of atomic centers; BL: bond length, BA: bond angle, DA: dihedral angle, OOP: out-of-plane. See Figure 2c of main text for atom numbering.
b) Linear combination coefficients appearing in definitions of non-redundant internal coordinates.

Table S4: Z-matrix definition of diacetylene. Distances in Å, angles in degrees.

Atomic symbol		BL[a]		BA[b]		DA[c]
H						
C	1	$r^{\dagger}_{C-H}$				
X	2	r_{C-X}	1	α_{90}		
C	2	$r^{\dagger}_{C-C}$	3	α_{90}	1	τ_{180}
X	4	r_{C-X}	2	α_{90}	3	τ_{180}
C	4	$r^{\dagger}_{C\equiv C}$	5	α_{90}	2	τ_{180}
X	6	r_{C-X}	4	α_{90}	5	τ_{180}
C	6	$r^{\dagger}_{C-C}$	7	α_{90}	4	τ_{180}
X	8	r_{C-X}	6	α_{90}	7	τ_{180}
H	8	$r^{\dagger}_{C-H}$	6	α_{90}	7	τ_{180}

r_{C-H} = 1.0613
r_{C-X} = 1.0000
r_{C-C} = 1.2077
$r_{C\equiv C}$ = 1.3734
α_{90} = 90.0
τ_{180} = 180.0

a) Z-matrix internal coordinates; BL: bond length, BA: bond angle, DA: dihedral angle. Graphical symbol † denotes internal coordinates employed in the fit. Output values of internal coordinates are reported.

Table S5: Z-matrix definition of ketene. Distances in Å, angles in degrees.

Atomic symbol		BL		BA		DA
X						
O	1	r_{O-X}				
C	2	$r^{\dagger}_{C=O}$	1	α_{90}		
X	3	r_{O-X}	2	α_{90}	1	τ_0
C	3	$r^{\dagger}_{C=C}$	4	α_{90}	1	τ_{180}
H	5	$r^{\dagger}_{C-H}$	3	$\alpha^{\dagger}_{HCC}$	4	τ_0
H	5	$r^{\dagger}_{C-H}$	3	$\alpha^{\dagger}_{HCC}$	4	τ_{180}

r_{O-X} = 1.0000
$r_{C=O}$ = 1.0606
$r_{C=C}$ = 1.3124
r_{C-H} = 1.0764
α_{90} = 90.0
α_{HCC} = 119.05
τ_0 = 0.0
τ_{180} = 180.0

a) Z-matrix internal coordinates; BL: bond length, BA: bond angle, DA: dihedral angle. Graphical symbol † denotes internal coordinates employed in the fit. Output values of internal coordinates are reported.

Table S6: Z-matrix definition of benzene. Distances in Å, angles in degrees.

Atomic symbol		BL		BA		DA
X						
C	1	$r^{\dagger}_{C-C}$				
C	1	$r^{\dagger}_{C-C}$	2	α_{60}		
C	1	$r^{\dagger}_{C-C}$	3	α_{60}	2	τ_{180}
C	1	$r^{\dagger}_{C-C}$	4	α_{60}	3	τ_{180}
C	1	$r^{\dagger}_{C-C}$	5	α_{60}	4	τ_{180}
C	1	$r^{\dagger}_{C-C}$	6	α_{60}	5	τ_{180}
H	3	$r^{\dagger}_{C-H}$	4	α_{120}	1	τ_{180}
H	4	$r^{\dagger}_{C-H}$	5	α_{120}	1	τ_{180}
H	5	$r^{\dagger}_{C-H}$	6	α_{120}	1	τ_{180}
H	6	$r^{\dagger}_{C-H}$	7	α_{120}	1	τ_{180}
H	7	$r^{\dagger}_{C-H}$	2	α_{120}	1	τ_{180}
H	2	$r^{\dagger}_{C-H}$	3	α_{120}	1	τ_{180}

r_{C-C} = 1.3916
r_{C-H} = 1.0799
α_{60} = 60.0
α_{120} = 120.0
τ_{180} = 180.0

a) Z-matrix internal coordinates; BL: bond length, BA: bond angle, DA: dihedral angle. Graphical symbol † denotes internal coordinates employed in the fit. Output values of internal coordinates are reported.

Table S7: Predicate observations used for fluorohydroxyborane, methenammine and nitric acid. Distances in Å, angles in degrees. See Figure 3 of main text for atom numbering.

	Predicate value	Assigned uncertainty
fluorohydroxyborane[a]		
r(B−H2)	1.1894	0.002
a(H2−B−F)	119.38	0.20
methenammine[b]		
r(C−H1)	1.0898	0.0010
r(C−H2)	1.0855	0.0010
a(H1−C−N)	124.324	0.200
a(H2−C−N)	118.683	0.200
nitric acid[c]		
r(N−O3)	1.2077	0.0020
r(N−O2)	1.1920	0.0020
r(O1−H)	0.9683	0.0010
r(O1−N−O3)	115.56	0.30
r(O1−N−O2)	114.20	0.20
r(N−O1−H)	102.18	0.20

a) Predicate values from Ref.[1]
b) Predicate values from Ref.[2]
c) Predicate values from Ref.[3]

Table S8: B2PLYP/VTZ and B3LYP/SNSD r_e structures of the Ip conformer of glycine. Distances in Å, angles in degrees. See Figure 4 of main text for atom numbering.

Coordinate	$r_e^{\text{B2PLYP/VTZ}}$	$r_e^{\text{B3LYP/SNSD}}$
r(C2−O2)	1.3528	1.3552
r(C2−O1)	1.2059	1.2091
r(O3−H5)	0.9677	0.9709
r(C1−C2)	1.5176	1.5244
r(C1−N)	1.4466	1.4497
r(C1−H3)	1.0905	1.0971
r(N−H1)	1.0109	1.0166
a(O1−C2−O2)	123.09	122.89
a(C1−C2−O2)	111.33	111.48
a(N−C1−C2)	115.47	115.88
a(H3−C1−C2)	107.55	107.51
a(H1−N−C1)	109.67	110.26
a(H5−O2−C2)	106.62	107.14
d(H4−C1−C2−O1)	123.30	123.41
d(H2−N−C1−C2)	57.67	58.27

References

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