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Cooperative Hydrogen Bonds Form a Pseudocycle Stabilising an Isolated Complex of Isocyanic Acid with Urea

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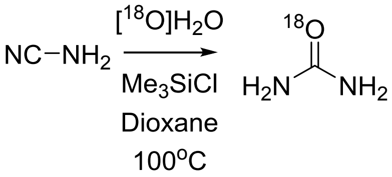
Method Applied to Synthesise [^{18}O]Urea



To [^{18}O]H_2O (2.0 mL, 100 mmol) in dry dioxane (12 mL) cooled in ice and stirred under nitrogen was added chlorotrimethylsilane (1.5 g, 1.08 mL, 13.8 mmol) dropwise. Cyanamide (1.20 g, 28.6 mmol) was added in portions and the mixture was heated at reflux for 80 min. After cooling to room temperature, methanol (10 mL) was added followed by sodium carbonate (1.0 g), and the mixture was stirred for 30 min. The resulting solid was removed by filtration and the filtrate was evaporated to give a white solid that was dried in vacuo. The solid was extracted with boiling acetone (3 × 15 mL), the extracts were combined and the solvent was remove. The remaining white solid was recrystallised from ethanol-diethyl ether (1:1, v/v) to yield large white crystals of the labelled urea (1.32 g, 74%): ^{1}H NMR (300 MHz, d^{6}-DMSO) δ 5.43 (bs, 4H, 2 x NH_2); ^{13}C NMR (175 MHz, D_2O) δ 162.45 (C^{18}O); ESI *m/z* 61.0 (^{16}O-MH^{+}, 6%), 62.9 (^{18}O-MH^{+}, 100%).

Method Applied to Measure Broadband Microwave Spectra

The instruments and methods employed have been described in detail previously.[1] A backing pressure of 6 bar is employed during pulsed injection of an argon buffer gas into a vacuum chamber. The generation of molecular complexes is achieved by laser-vaporising material from a solid target such that it becomes entrained in this buffer gas which undergoes supersonic expansion. The frequency doubled output of a Nd:YAG laser (532 nm, 20 mJ pulse^{-1}, 10 ns duration) is focussed on the target which is continually rotated and translated to ensure fresh surface material is exposed to each laser pulse. Target rods were prepared using a 1:1 molar ratio of urea and copper, using a table top press and an evacuable pellet die (Specac). The molar ratio of urea and copper was maintained during the experiments involving synthetically enriched ^{13}C, ^{18}O, ^{15}N and deuterium containing urea.

An arbitrary waveform generator (AWG) is used to supply a chirped microwave pulse that sweeps from 0.5–12 GHz over a duration of 1 μs. This chirped pulse passes through a 12.2 GHz low-pass filter and is mixed against the filtered output of a phase-locked dielectric resonant oscillator (PDRO) that supplies a 19.00 GHz signal. The AWG and PDRO are each phase-locked to a 10 MHz frequency accurate to 1 part in 10^{11}. The output after mixing passes through a 7–18.5 GHz bandpass filter and is amplified prior to irradiation of the molecular sample. The data presented herein were acquired using a 300W travelling wave tube amplifier. The microwave frequency sweep is introduced perpendicular to the propagation direction of the expanding gas via a microwave horn. The molecular emission signal (free induction decay, or FID, of the polarisation) is detected by a second horn antenna and amplified by a low noise amplifier. The FID is mixed down against the 19.00 GHz reference signal supplied by the PDRO and then passes through a 12.5 GHz low-pass filtered before detection. Each FID is measured over a 20 μs period following each chirped polarisation pulse. A fast digital oscilloscope is phase-locked to the same 10 MHz external frequency reference used by the PDRO and AWG and used to digitise the molecular FID. The above sequence of microwave polarisation pulse, detection and recording of FID is repeated eight times following each individual nozzle (i.e. gas sample introduction) pulse to maximise the duty cycle of the spectrometer. In order to record the spectrum of urea-HNCO during this study, 3.9 million FIDs (acquired from 487k valve pulses) were co-added in the time domain. FID's are averaged in the time domain before Fourier transforming to yield the frequency domain spectrum spanning from 7 to 18.5 GHz. After application of a Kaiser-Bessel window function, all observed transitions have a full width at half maximum (FWHM) of 150 kHz.

Ab Initio Calculations

Calculations were performed at the CCSD(T)(F12*) level of theory, that is, explicitly correlated coupled-cluster singles, doubles and perturbative triples[2] with the (F12*) approximation of Haettig, Tew and Koehn.[3] Only valence electrons were correlated and calculations were performed using the aug-cc-pVDZ or aug-cc-pVTZ basis sets.[4] The exponent of the correlation factor was 1 a_0,[5] the F12 method 2B was used,[6] and the details of the auxiliary basis sets were that the aug-cc-pVTZ Coulomb fitting basis[7] was used as CABS[8]; and the aug-cc-pwCVQZ Coulomb fitting basis[9] and the aug-cc-pVTZ JK fitting basis were used for density fitting the correlation and Fock integrals, respectively. Structures of HNCO, urea and the lowest energy complex were optimised at the CCSD(T)(F12*) level of theory, first using the aug-cc-pVDZ basis and then the aug-cc-pVTZ basis set. At the optimised CCSD(T)(F12*)/aug-cc-pVTZ structures of HNCO, urea and the hydrogen-bonded complex, harmonic frequencies were evaluated at the CCSD(T)(F12*)/aug-cc-pVDZ level of theory. The force constant matrix was computed numerically using a five point formula. Residual basis set incompleteness errors led to an imaginary frequency for the out-of-plane intermolecular vibration in the complex. To refine the harmonic frequencies, CCSD(T)(F12*)/aug-cc-pVTZ calculations were therefore performed: a 5-point formula was used for each mode individually, involving displacements along the normal mode vector from the CCSD(T)(F12*)/aug-cc-pVDZ Hessian. The harmonic wavenumbers are reported in Supplementary Data Table 6 together with their vibrational characteristics.

Supplementary Data : Table 1

Spectroscopic parameters determined by fitting parameters in the model Hamiltonian to measured transition frequencies.

	A_0 / MHz	B_0 / MHz	C_0 / MHz	D_{JK} / kHz	D_J / kHz	d_1 / Hz	d_2 / Hz		σ / k
$(H_2N)_2CO$□$HNCO$	10381.29(86)[a]	828.69158(86)	769.17039(84)	2.	0.1723(15)	-15	-3.27(87)		
$(H_2N)_2CO$□$DNCO$	10322.7(20)	827.9540(13)	768.3274(17)	[2.	0.1851(52)	[-15	[-3.27][b]		
$(D_2N)_2CO$□$HNCO$	8924.24(91)	789.79282(98)	727.5205(14)	[2.	0.1634(41)	[-15	[-3.27]		
$(D_2N)_2CO$□$DNCO$	8879.52(47)	788.94455(30)	726.58757(36)	3.	0.1511(12)	[-15	[-3.27]		
$(H_2{}^{14}N)_2CO$□$H^{15}NCO$	10356.7(43)	825.7593(26)	766.5828(21)	3.	0.1787(45)	-20	[-3.27]		
$(H_2{}^{15}N)_2CO$□$H^{14}NCO$	10031.4(14)	812.59953(52)	753.39136(60)	3.	0.1746(21)	[-15	[-3.27]		
$(H_2{}^{15}N)_2CO$□$H^{15}NCO$	10020.1(12)	809.60349(42)	750.76755(44)	2.	0.1759(17)	[-15	[-3.27]		
$(H_2N)_2{}^{13}CO$□$HN^{13}CO$	10381.67(89)	814.80928(66)	757.19655(71)	2.	0.1812(12)	-14	[-3.27]		
$(H_2N)_2{}^{12}CO$□$HN^{13}CO$	10384.9(43)	819.3670(23)	761.1312(31)	2.	0.1783(51)	-13	[-3.27]		
$(H_2N)_2{}^{13}CO$□$HN^{12}CO$	10384.4(52)	824.1559(23)	765.2601(25)	2.	0.1771(50)	-15	[-3.27]		
$(H_2N)_2C^{18}O$□$HNC^{18}O$	9995.1(14)	788.9338(18)	732.8396(14)	2.	0.1606(28)	-15	[-3.27]		
$(H_2N)_2C^{16}O$□$HNC^{18}O$	10364.2(16)	791.7175(17)	737.1810(23)	2.	0.1555(29)	-20	[-3.27]		
$(H_2N)_2C^{18}O$□$HNC^{16}O$	10007.0(15)	826.0415(19)	764.7768(22)	2.	0.1848(35)	-19	[-3.27]		

[a] Numbers in parentheses are one standard deviation in units of the last significant figure.

[b] Fixed to the value determined for $(H_2N)_2CO$□$HNCO$.

Supplementary Data : Table 2

Comparison of fitted rotational constants and derived planar moments with results calculated *ab initio* at the CCSD(T)(F12*) / AVTZ level.

	A_0 [A_e]/ MHz	B_0 [B_e]/ MHz	C_0 [C_e]/ MHz	P_a / uÅ^2	P_b / uÅ^2	P_c / uÅ^2
$(H_2N)_2CO$□$HNCO$	10381.29(86)[a] [10340.09]	828.69158(86) [835.6421]	769.17039(84) [775.02613]	609.10(5) [603.91]	47.94(5) [48.09]	0.7446(8) [0.7875]
$(H_2N)_2CO$□$DNCO$	10322.7(20) [10334.7]	827.9540(13) [828.0865]	768.3247(17) [768.4398]	610.0(5) [609.5]	48.2(3) [48.1]	0.753(6) [0.765]
$(D_2N)_2CO$□$HNCO$	8924.24(91) [8922.5]	789.79282(98) [795.4539]	727.5205(14) [732.2903]	639.3(1) [634.4]	55.8(2) [55.7]	0.961(2) [0.92]
$(D_2N)_2CO$□$DNCO$	8879.52(86) [8898.19]	788.94455(78) [794.73504]	726.58757(83) [731.51930]	639.61(6) [634.99]	55.95(6) [55.87]	0.970(1) [0.921]
$(H_2{}^{14}N)_2CO$□$H^{15}NCO$	10356.7(43) [10323.5]	825.7593(26) [832.7488]	766.5828(21) [772.4470]	611.2(3) [606.1]	48.0(3) [48.17]	0.776(4) [0.789]
$(H_2{}^{15}N)_2CO$□$H^{14}NCO$	10031.4(14) [9991.7]	812.59953(52) [819.26623]	753.39136(60) [759.0412]	621.6(7) [616.05]	49.65(8) [49.76]	0.752(1) [0.818]
$(H_2{}^{15}N)_2CO$□$H^{15}NCO$	10020.1(12) [9976.98]	809.60349(42) [816.31496]	750.76755(44) [756.42543]	623.84(4) [618.28]	49.70(4) [49.84]	0.768(7) [0.8189]
$(H_2N)_2{}^{13}CO$□$HN\ {}^{13}CO$	10381.67(89) [10338.8]	814.80928(66) [821.60904]	757.19655(71) [762.93555]	619.87(6) [614.32]	47.97(6) [48.1]	0.748(1) [0.788]
$(H_2N)_2{}^{12}CO$□$HN\ {}^{13}CO$	10384.9(43) [10340.0]	819.3670(23) [826.2140]	761.1312(31) [766.9100]	616.1(3) [610.89]	47.9(3) [48.1]	0.737(4) [0.789]
$(H_2N)_2{}^{13}CO$□$HN\ {}^{12}CO$	10384.4(52) [10338.9]	824.1559(23) [831.0594]	765.2601(25) [771.0772]	612.8(5) [607.3]	48.0(5) [48.1]	0.736(7) [0.788]
$(H_2N)_2C^{18}O$□$HNC^{18}O$	9995.1(14) [9951.0]	788.9338(18) [795.3689]	732.8396(14) [738.2429]	639.82(9) [634.59]	49.8(9) [49.9]	0.765(1) [0.809]
$(H_2N)_2C^{16}O$□$HNC^{18}O$	10364.2(16) [10331.0]	791.7175(17) [798.25039]	737.1810(23) [742.7120]	637.9(2) [632.3]	48.0(2) [48.1]	0.769(3) [0.788]
$(H_2N)_2C^{18}O$□$HNC^{16}O$	10007.0(15) [9958.9]	826.0415(19) [832.8822]	764.7768(22) [770.4973]	611.06(9) [605.97]	49.76(9) [49.94]	0.746(1) [0.809]

[a] Numbers in parentheses are one standard deviation in units of the last significant figure.

Supplementary Data : Table 3

Atomic coordinates determined by various methods of structure determination. Atoms internal to isocyanic acid are labelled with subscript "A" while those internal to urea are labelled with subscript "B".

	a / Å	b / Å	c / Å	
O_B	0.9976(24) 1.0026 1.033(8)	–0.9613(25) –0.9715 –0.991(8)	0.000(40)[a] 0.1058 0.10644(1)	r_s *Ab initio,* r_e r_0
C_B	1.8395(21) 1.8319 1.8419(6)	0.00(9)[a] –0.0716 –0.080(1)	0.00(6)[a] 0.0225 0.0221(2)	r_s *Ab initio,* r_e r_0
H_A	–0.7387(49) –0.6645 –0.732(2)	–0.4220(85) –0.3714 –0.387(9)	0.072(50) 0.0332 0.033(1)	r_s *Ab initio,* r_e r_0
N_A	–1.4762(27) –1.4582 –1.469(1)	0.259(15) 0.2802 0.278(6)	–0.131(30) –0.0350 –0.0351(4)	r_s *Ab initio,* r_e r_0
C_A	–2.6410(14) –2.6353 –2.6469(1)	–0.087(44) –0.0054 –0.0132(9)	–0.109(35) –0.0207 –0.0207(2)	r_s *Ab initio,* r_e r_0
O_A	–3.80462(62) –3.7958 –3.8058(6)	–0.158(15) –0.1506 –0.146(4)	–0.111(21) –0.0195 –0.0209(3)	r_s *Ab initio,* r_e r_0

[a] Numbers in parentheses are one standard deviation in units of the last significant figure.

[b.] Imaginary coordinates were obtained and are therefore fixed at zero.

Supplementary Data : Table 4

Experimentally-determined[10,11] r_s and *ab initio* calculated, r_e, geometries of the isolated molecules, HNCO and $(NH_2)_2CO$.

	r_s	r_e (CCSD(T)(F12*) / AVDZ)	r_e (CCSD(T)(F12*) / AVTZ
HNCO			
r(C–O) / Å	1.1664	1.165	1.165
r(N–C) / Å	1.2140	1.217	1.217
r(H–N) / Å	0.995	1.005	1.005
$\angle$(N–C–O) / °	172.6	172.4	172.4
$\angle$(H–N–C) / °	123.9	123.5	123.3
$\angle$(H–N–C–O) / °	180	180	180
Urea[a]	r_s/r_0		
r(C=O) / Å	1.2211	1.213	1.213
r(C–N) / Å	1.3779	1.383	1.383
r(C–N) / Å	1.3779	1.383	1.383
$\angle$(N–C–O) / °	122.64	123.1	123.1
$\angle$(N–C–N) / °	114.71	113.8	113.8
r(N–H) / Å	1.0212	1.006	1.006
$\angle$(H–N–C) / °	112.8	112.9	112.8
$\angle$(H–N–C–O) / °	10.8	13.7	14.0
r(N–H) / Å	0.9978	1.006	1.006
$\angle$(H–N–C) / °	119.2	117.2	117.1
$\angle$(H–N–C–O) / °	156.9	150.3	150.2
r(N–H) / Å	1.0212	1.006	1.006
$\angle$(H–N–C) / °	112.8	112.9	112.8
$\angle$(H–N–C–O) / °	10.8	13.7	14.0
r(N–H) / Å	0.9978	1.006	1.006
$\angle$(H–N–C) / °	119.2	117.2	117.1
$\angle$(H–N–C–O) / °	156.9	150.3	150.2

[a] r_s/r_0 parameters reproduced from Ref. 11.

Supplementary Data : Table 5

Details of fit to determine structural parameters of $(H_2N)_2CO$□HNCO. Fitted parameters are indicated in bold font.

	r_s / r_0	CCSD(T)(F12*) / AVDZ	CCSD(T)(F12*) / AVTZ
HNCO[a]			
r(C–O) / Å	[1.1664]	1.170	1.170
r(N–C) / Å	[1.2140]	1.213	1.211
r(H–N) / Å	[0.995]	1.030	1.029
∠(N–C–O) / °	[172.6]	173.4	173.5
∠(H–N–C) / °	[123.9]	126.5	126.8
∠(H–N–C–O) / °	[180]	180	180
Urea[a]			
r(C=O) / Å	[1.221]	1.228	1.227
r(C–N) / Å	[1.378]	1.375	1.373
r(C–N) / Å	[1.378]	1.369	1.368
∠(N–C–O) / °	[122.64]	121.7	121.7
∠(N–C–N) / °	[114.71]	115.2	115.2
r(N–H) / Å	[1.021]	1.006	1.006
∠(H–N–C) / °	[113.7][b]	113.7	113.7
∠(H–N–C–O) / °	[13.3][b]	13.2	13.3
r(N–H) / Å	[0.998]	1.006	1.005
∠(H–N–C) / °	[118.2][b]	118.2	118.2
∠(H–N–C–O) / °	[153.5][b]	153.5	153.5
r(N–H) / Å	[1.021]	1.009	1.008
∠(H–N–C) / °	[115.5][b]	115.5	115.5
∠(H–N–C–O) / °	[12.2][b]	12.1	12.2
r(N–H) / Å	[0.998]	1.005	1.004
∠(H–N–C) / °	[118.4][b]	118.4	118.4
∠(H–N–C–O) / °	[156.9][b]	156.5	156.9
Intermolecular[c]			
r($\mathrm{O_B}$□$\mathrm{H_A}$) / Å	**1.866(11)**	1.775	1.773
∠($\mathrm{N_AH_A}$□$\mathrm{O_B}$) / °	**156.8(6)**	160.3	160.4
∠($\mathrm{C_BO_B}$□$\mathrm{H_A}$) / °	**112.5(8)**	112.6	112.6
∠($\mathrm{O_B}$□$\mathrm{H_AN_AC_A}$) / °	[180]	180	180
∠($\mathrm{C_BO_B}$□$\mathrm{H_AN_A}$) / °	[0.46][b]	0.54	0.46
∠($\mathrm{N_BC_BO_B}$□$\mathrm{H_A}$) / °	[169.7][b]	169.8	169.7

[a] All bond lengths internal to the monomer sub-units, HNCO and urea are fixed to values[10,11] appropriate to either the r_s geometry of HNCO or the r_s/r_0 geometry of urea. ∠(N–C–O) and ∠(N–C–N) are fixed to their values for the isolated urea monomer.

[b] Parameter fixed to the result calculated at the CCSD(T)(F12*) / AVTZ level.

[c] Subscripts are added to clarify the identity of the atoms used to define intermolecular coordinates. Atoms internal to isocyanic acid are labelled with subscript “A” while those internal to urea are labelled with subscript “B”.

Supplementary Data Table 6:
Ab initio calculated harmonic vibrational wavenumbers (in cm^{-1}) of $(H_2N)_2CO$□HNCO, urea and HCNO. Gas phase experimental fundamental wavenumbers for HNCO are also presented.

Mode	**$(H_2N)_2CO$□HNCO**		**$(H_2N)_2CO$**	**HNCO**		**Mode description**
	DZ	**TZ**	**DZ**	**DZ**	**Experimental**	
1	3729	3717	3717			NH asym str (8,9)
2	3716	3705	3717			NH asym str (10,11)
3	3608	3598	3602			NH sym str (8,9)
4	3587	3576	3599			NH sym str (10,11)
5	3257	3242		3705	3538^a	NH str
6	2318	2310		2316	2269^b	CO str
7	1777	1770	1815			CO str
8	1660	1657	1646			NHH bend (10,11)
9	1643	1640	1641			NHH bend (8,9)
10	1466	1464	1428			CN asym str
11	1325	1319		1320	1327^c	CN str
12	1192	1189	1191			NH_2 rock sym
13	1070	1072	1063			NH_2 rock asym
14	991	986	961			CN sym str
15	965	971		814	777^d	CNH bend
16	786	788	790			C out of plane
17	721	723				OH out of plane
18	665	668		640	656^e	OCN bend
19	609	611	583			OCN bend
20	580	581	574			OCN bend
21	547	548		571	577^d	OCN bend
22	515	518	540			NH bend
23	487	491	475			NH bend
24	410	432	443			NH bend
25	365	369	372			NH bend
26	192	202				OH...O str
27	111	112				O...HN str
28	85	64				/ \ bend
29	63	65				/ / bend
30	--	26				Out of plane bend

a: Ref [12], b: Ref [13], c: Ref [14], d: Ref [15],.e: Ref: [16]

Supplementary Data : Table 7

List of measured transition frequencies and obs.– calc. transition frequencies.

$(H_2N)_2CO$ --- HNCO

J''	K_a''	K_c''	J'	K_a'	K_c'	Observed	Obs-Calc
6	1	6	5	1	5	9406.232	-0.013
6	0	6	5	0	5	9577.322	-0.004
6	1	5	5	1	4	9763.299	-0.001
7	1	7	6	1	6	10972.860	-0.008
7	0	7	6	0	6	11169.291	-0.000
7	2	6	6	2	5	11182.505	0.012
7	2	5	6	2	4	11197.973	-0.018
7	1	6	6	1	5	11389.371	-0.002
8	1	8	7	1	7	12539.009	0.007
8	0	8	7	0	7	12759.314	0.009
8	2	7	7	2	6	12778.983	-0.004
8	2	6	7	2	5	12802.211	-0.000
8	1	7	7	1	6	13014.905	-0.001
9	1	9	8	1	8	14104.594	0.009
9	0	9	8	0	8	14347.111	0.008
9	2	8	8	2	7	14375.082	0.003
9	2	7	8	2	6	14408.219	0.008
9	1	8	8	1	7	14639.815	0.001
10	1	10	9	1	9	15669.563	0.005
10	0	10	9	0	9	15932.435	0.004
10	2	9	9	2	8	15970.723	0.003
10	4	6	9	4	5	15980.599	-0.005
10	4	7	9	4	6	15980.599	-0.002
10	2	8	9	2	7	16016.192	0.002
10	1	9	9	1	8	16264.012	0.001
11	1	11	10	1	10	17233.857	-0.010
11	0	11	10	0	10	17515.041	-0.008
11	2	10	10	2	9	17565.852	-0.007
11	3	9	10	3	8	17582.714	0.007
11	3	8	10	3	7	17583.749	0.007
11	2	9	10	2	8	17626.331	-0.002
11	1	10	10	1	9	17887.397	-0.005

$(H_2N)_2{}^{12}CO$ --- HN ^{13}CO

J''	K_a''	K_c''	J'	K_a'	K_c'	Observed	Obs-Calc
7	0	7	6	0	6	11048.406	-0.011
7	1	6	6	1	5	11263.498	0.006
8	0	8	7	0	7	12621.417	0.015
8	1	7	7	1	6	12871.098	-0.007
9	2	7	8	2	6	14250.725	-0.005
9	1	8	8	1	7	14478.118	0.000
10	1	10	9	1	9	15502.790	-0.007
10	0	10	9	0	9	15760.767	0.009
10	1	9	9	1	8	16084.447	-0.001
11	0	11	10	0	10	17326.649	-0.004
11	2	9	10	2	8	17433.138	0.007
11	1	10	10	1	9	17690.003	-0.004

$(H_2N)_2{}^{13}CO$ --- HN ^{13}CO

J''	K_a''	K_c''	J'	K_a'	K_c'	Observed	Obs-Calc
6	0	6	5	0	5	9422.810	0.004
6	1	5	5	1	4	9602.583	0.004
7	0	7	6	0	6	10989.287	0.003
8	0	8	7	0	7	12553.929	-0.002
8	1	7	7	1	6	12800.777	-0.001
9	1	9	8	1	8	13880.943	-0.000
9	0	9	8	0	8	14116.498	0.000
9	2	7	8	2	6	14173.683	-0.003
9	1	8	8	1	7	14399.029	-0.008
10	1	10	9	1	9	15421.186	-0.004
10	0	10	9	0	9	15676.746	0.001
10	2	8	9	2	7	15755.146	0.002
10	1	9	9	1	8	15996.627	0.000
10	1	9	9	1	8	15996.627	0.000
11	1	11	10	1	10	16960.808	0.001
11	0	11	10	0	10	17234.444	-0.001
11	2	10	10	2	9	17282.030	0.001
11	2	9	10	2	8	17338.630	0.001
11	1	10	10	1	9	17593.463	0.002
12	1	12	11	1	11	18499.747	0.001

$(H_2N)_2{}^{13}CO$ --- $HN\,{}^{12}CO$

J''	K_a''	K_c''	J'	K_a'	K_c'	Observed	Obs - Calc
7	1	6	6	1	5	11328.144	0.003
7	0	7	6	0	6	11110.472	-0.027
8	1	8	7	1	7	12474.043	-0.008
8	0	8	7	0	7	12692.244	0.013
8	1	7	7	1	6	12944.955	-0.002
9	1	8	8	1	7	14561.169	0.009
9	0	9	8	0	8	14271.811	0.017
9	1	9	8	1	8	14031.561	0.012
10	1	9	9	1	8	16176.654	-0.011
11	1	10	10	1	9	17791.386	0.005
11	0	11	10	0	10	17423.415	-0.009
11	2	9	10	2	8	17532.344	-0.001
11	1	11	10	1	10	17144.693	-0.002

$(H_2{}^{14}N)_2CO$ --- $H{}^{15}NCO$

J''	K_a''	K_c''	J'	K_a'	K_c'	Observed	Obs-Calc
7	1	7	6	1	6	10935.442	-0.016
7	0	7	6	0	6	11130.797	0.010
8	1	8	7	1	7	12496.251	-0.009
8	0	8	7	0	7	12715.371	0.021
8	2	6	7	2	5	12757.811	-0.004
8	1	7	7	1	6	12969.386	-0.001
9	0	9	8	0	8	14297.726	0.011
9	2	7	8	2	6	14358.215	0.008
9	1	8	8	1	7	14588.593	-0.024
10	1	10	9	1	9	15616.177	0.010
10	0	10	9	0	9	15877.625	-0.006
10	2	8	9	2	7	15960.562	0.004
10	1	9	9	1	8	16207.139	0.002
11	1	11	10	1	10	17175.152	-0.006
11	0	11	10	0	10	17454.857	-0.004
11	1	10	10	1	9	17824.863	0.005

$(H_2{}^{15}N)_2CO$ --- $H{}^{14}NCO$

J''	K_a''	K_c''	J'	K_a'	K_c'	Observed	Obs-Calc
6	0	6	5	0	5	9385.862	0.009
6	1	5	5	1	4	9571.057	-0.013
7	1	7	6	1	6	10750.779	0.012
7	0	7	6	0	6	10945.798	-0.002

7	2	6	6	2	5	10959.296	-0.018
7	1	6	6	1	5	11165.071	-0.005
8	1	8	7	1	7	12285.147	0.008
8	0	8	7	0	7	12503.748	-0.001
8	2	7	7	2	6	12523.879	-0.021
8	1	7	7	1	6	12758.522	-0.006
9	1	9	8	1	8	13818.947	-0.001
9	0	9	8	0	8	14059.435	0.008
9	2	8	8	2	7	14088.098	0.022
9	2	7	8	2	6	14122.044	0.007
9	1	8	8	1	7	14351.336	-0.003
10	1	10	9	1	9	15352.133	0.000
10	0	10	9	0	9	15612.576	-0.001
10	2	9	9	2	8	15651.786	-0.002
10	1	9	9	1	8	15943.43	0.011
11	1	11	10	1	10	16884.635	-0.003
11	0	11	10	0	10	17162.956	0.000
11	2	10	10	2	9	17214.995	0.008
11	2	9	10	2	8	17276.959	-0.001
11	1	10	10	1	9	17534.672	0.001
12	1	12	11	1	11	18416.398	-0.014

$(H_2{}^{15}N)_2CO$ --- $H^{15}NCO$

J''	K_a''	K_c''	J'	K_a'	K_c'	Observed	Obs-Calc
5	1	5	4	1	4	7653.441	-0.005
5	0	5	4	0	4	7796.146	-0.004
5	1	4	4	1	3	7947.576	0.001
6	1	6	5	1	5	9183.337	0.006
6	0	6	5	0	5	9352.243	-0.005
6	1	5	5	1	4	9536.250	-0.006
7	1	7	6	1	6	10712.779	-0.006
7	0	7	6	0	6	10906.649	0.004
7	2	6	6	2	5	10920.032	0.009
7	1	6	6	1	5	11124.469	-0.006
8	1	8	7	1	7	12241.744	0.002
8	0	8	7	0	7	12459.068	0.003
8	2	7	7	2	6	12479.011	0.004
8	1	7	7	1	6	12712.151	0.003
9	1	9	8	1	8	13770.142	0.001
9	0	9	8	0	8	14009.240	0.000
9	2	8	8	2	7	14037.579	-0.006
9	1	8	8	1	7	14299.194	0.005
10	1	10	9	1	9	15297.917	-0.003

10	0	10	9	0	9	15556.913	-0.001
10	1	9	9	1	8	15885.514	0.006
11	1	11	10	1	10	16825.026	0.001
11	0	11	10	0	10	17101.851	0.005
11	2	10	10	2	9	17153.308	-0.007
11	2	9	10	2	8	17214.577	0.004
11	1	10	10	1	9	17471.004	-0.007
12	1	12	11	1	11	18351.402	-0.000

$(H_2N)_2C^{16}O$ --- $HNC^{18}O$

J''	K_a''	K_c''	J'	K_a'	K_c'	Observed	Obs-Calc
7	1	6	6	1	5	10889.786	-0.010
8	0	8	7	0	7	12211.396	0.005
8	1	7	7	1	6	12444.207	0.005
9	2	7	8	2	6	13783.037	0.005
10	1	10	9	1	9	15006.645	-0.008
10	0	10	9	0	9	15250.202	-0.006
10	1	9	9	1	8	15551.370	0.003
11	1	11	10	1	10	16505.094	0.009
11	1	10	10	1	9	17103.977	0.001
12	0	12	11	0	11	18279.894	0.000
12	2	11	11	2	10	18335.000	-0.001
12	2	10	11	2	9	18400.767	-0.003

$(H_2N)_2C^{18}O$ --- $HNC^{16}O$

J''	K_a''	K_c''	J'	K_a'	K_c'	Observed	Obs-Calc
7	0	7	6	0	6	11118.395	0.006
8	0	8	7	0	7	12700.557	-0.010
8	1	7	7	1	6	12964.919	-0.000
9	1	9	8	1	8	14032.541	-0.004
9	0	9	8	0	8	14280.316	0.006
9	2	7	8	2	6	14347.674	0.008
9	1	8	8	1	7	14583.372	-0.004
10	1	9	9	1	8	16201.042	-0.003
11	0	11	10	0	10	17431.407	0.004
11	2	10	10	2	9	17487.377	-0.004
11	2	9	10	2	8	17553.951	-0.001
11	1	10	10	1	9	17817.824	0.003

$(H_2N)_2C^{18}O$ --- $HNC^{18}O$

J''	K_a''	K_c''	J'	K_a'	K_c'	Observed	Obs-Calc
8	1	8	7	1	7	11944.447	-0.005
8	1	8	7	1	7	11944.448	-0.004
8	0	8	7	0	7	12152.435	-0.005
8	1	7	7	1	6	12392.962	0.003
9	1	9	8	1	8	13435.847	-0.009
9	0	9	8	0	8	13664.936	0.002
9	2	7	8	2	6	13721.268	0.016
9	1	8	8	1	7	13940.265	-0.012
10	1	10	9	1	9	14926.709	0.013
10	0	10	9	0	9	15175.161	0.013
10	2	8	9	2	7	15252.336	-0.016
11	1	11	10	1	10	16416.916	-0.006
11	0	11	10	0	10	16682.877	0.016
11	2	10	10	2	9	16729.693	-0.005
11	2	9	10	2	8	16785.467	0.018
11	1	10	10	1	9	17032.854	-0.005
12	1	12	11	1	11	17906.481	-0.004
12	0	12	11	0	11	18187.859	-0.007
12	2	11	11	2	10	18248.448	-0.002
12	2	10	11	2	9	18320.698	-0.002

$(H_2N)_2CO$ --- DNCO

J''	K_a''	K_c''	J'	K_a'	K_c'	Observed	Obs-Calc
7	0	7	6	0	6	11158.064	0.014
7	1	6	6	1	5	11378.594	-0.022
8	0	8	7	0	7	12746.404	-0.004
8	2	6	7	2	5	12789.743	-0.008
8	1	7	7	1	6	13002.597	0.003
9	0	9	8	0	8	14332.543	0.012
9	2	7	8	2	6	14394.217	-0.013
9	1	8	8	1	7	14625.938	-0.002
10	1	10	9	1	9	15653.072	0.009
10	0	10	9	0	9	15916.167	0.006
10	2	8	9	2	7	16000.711	0.012
10	2	8	9	2	7	16000.713	0.014
11	1	11	10	1	10	17215.667	-0.022
11	1	10	10	1	9	17870.372	-0.002

$(D_2N)_2CO$ --- HNCO

J''	K_a''	K_c''	J'	K_a'	K_c'	Observed	Obs-Calc

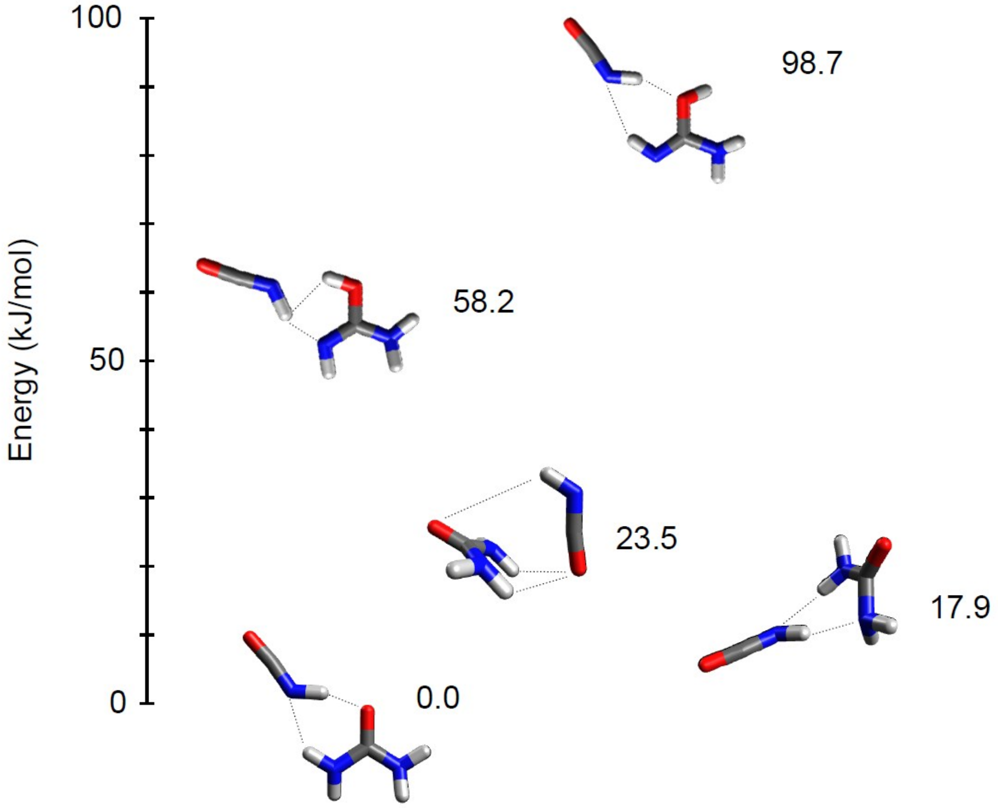
7	0	7	6	0	6	10601.068	0.006
7	1	6	6	1	5	10834.127	0.008
8	1	7	7	1	6	12379.901	-0.016
9	1	9	8	1	8	13365.111	0.010
9	1	8	8	1	7	13924.908	-0.008
10	1	10	9	1	9	14847.389	0.021
10	2	8	9	2	7	15221.513	0.014
11	1	11	10	1	10	16328.820	0.003
11	0	11	10	0	10	16612.117	-0.013
11	2	9	10	2	8	16754.546	-0.006
12	1	12	11	1	11	17809.375	-0.012
12	0	12	11	0	11	18106.446	0.016
12	2	10	11	2	9	18290.513	-0.005

$(D_2N)_2CO$ --- DNCO

J''	K_a''	K_c''	J'	K_a'	K_c'	Observed	Obs-Calc
6	0	6	5	0	5	9080.506	-0.003
6	1	5	5	1	4	9277.168	-0.008
7	0	7	6	0	6	10588.452	0.001
7	1	6	6	1	5	10821.909	-0.002
8	1	8	7	1	7	11867.471	-0.009
8	0	8	7	0	7	12093.894	0.005
8	2	6	7	2	5	12149.413	0.001
8	1	7	7	1	6	12365.960	0.006
9	1	9	8	1	8	13348.656	-0.000
9	0	9	8	0	8	13596.485	-0.010
9	2	7	8	2	6	13675.514	0.009
9	1	8	8	1	7	13909.194	0.001
10	1	10	9	1	9	14829.080	0.008
10	0	10	9	0	9	15095.971	0.015
10	2	9	9	2	8	15145.410	-0.011
10	2	8	9	2	7	15204.135	-0.001
10	1	9	9	1	8	15451.512	0.002
11	1	11	10	1	10	16308.662	0.002
11	0	11	10	0	10	16591.992	-0.000
11	2	10	10	2	9	16657.533	0.006
11	2	9	10	2	8	16735.514	-0.005
11	1	10	10	1	9	16992.780	-0.002
12	1	12	11	1	11	17787.360	-0.003
12	0	12	11	0	11	18084.350	-0.006
12	2	11	11	2	10	18168.941	0.002
12	2	10	11	2	9	18269.832	-0.000

Supplementary Data : Figure 1

Relative energies (kJ mol^{-1}) of alternative geometries of $(NH_2)_2CO$□$HNCO$ calculated *ab initio* at the MP2/aug-cc-pVTZ level.



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