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A molecular dynamics study of the effects of fast molecular motions on solid-state NMR parameters

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Supporting information

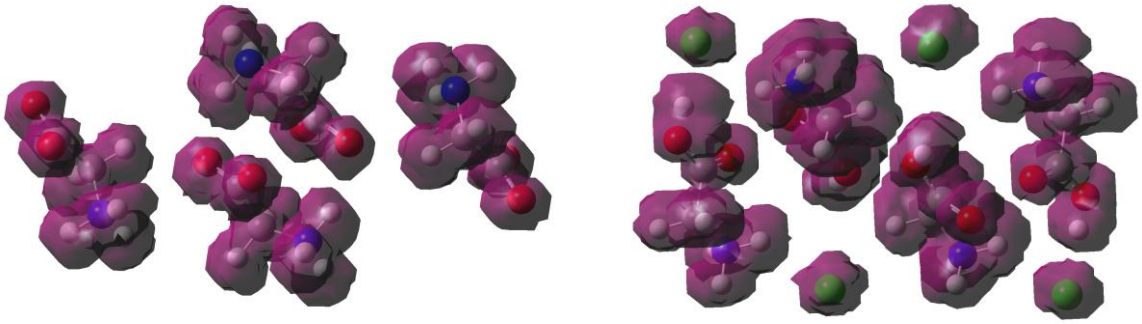

Figure S1. The space explored by α-glycine (left) and glycine hydrochloride (right) nuclei during the MD simulation.

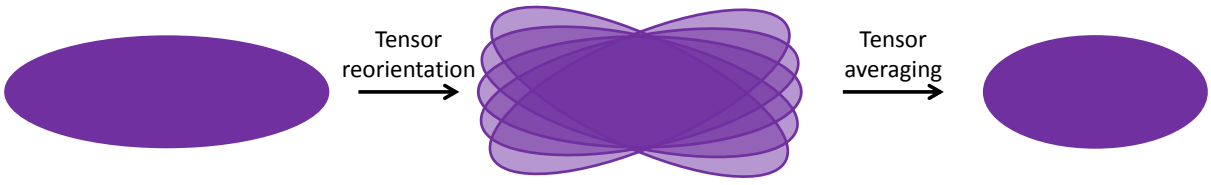

Figure S2. Graphical representation of the averaging of NMR tensors.

Glutamic acid hydrochloride

In the case of glutamic acid hydrochloride a large discrepancy between calculated and experimental quadrupolar coupling was noted for one particular oxygen. As seen in Table S1, the magnitude of the quadrupolar coupling of oxygen O4 calculated from the neutron diffraction structure without optimisation is rather far from the experimental value even when dynamics are included. The calculated force on the hydrogen atom attached to the oxygen atom O4 is rather high (1.22 ev/Å). Optimising the position of this hydrogen atom increases the O4–H bond distance by 0.04 Å, and the C-O-H valence angle decreases by 2.6° (see Table S1). The calculated oxygen quadrupolar coupling for O4 with the MD correction (–7.64 MHz) was much closer to the experimental value using this partially optimised structure. In addition the experimental difference between the O4 and O1 isotropic chemical shifts (21.4 ppm) is much better reproduced using the new (22.3 ppm) rather than original neutron structure (10.5 ppm). Note that the calculated carbon chemical shifts were barely changed (less than 0.7 ppm) by the hydrogen atom position optimisation.

Table S1. Calculated and experimental ^{17}O quadrupolar couplings and O–H distances in glutamic acid hydrochloride.

	CSD	CSD+MD	OptH+MD	Exp[1]
C_Q(O1) / MHz	-7.41	-7.33	-7.33	7.45±0.05
C_Q(O2) / MHz	8.40	8.40	8.40	8.16±0.05
C_Q(O3) / MHz	8.69	8.50	8.44	8.31±0.05
C_Q(O4) / MHz	-8.13	-7.91	-7.64	7.49±0.05
d(O4–H) / Å	0.981		1.016	
angle C5-O4-H / °	114.7		112.1	

Table S2. The calculated static NMR parameters and MD-induced changed of the parameters for glycine hydrochloride. The atom numbering is identical to that in the crystallographic database.

		σ_{iso} [ppm]	$\Delta\delta$ [ppm]	η	χ [MHz]	η_Q	$\Delta\sigma_{iso}$ [ppm]	$\Delta\Delta\delta$ [ppm]	$\Delta\eta$	$\Delta\chi$ [MHz]	$\Delta\eta_Q$
H	1	21.49	28.01	0.06	0.19	0.04	-1.01	-1.70	-0.01	-0.03	0.00
H	2	21.58	27.99	0.11	0.19	0.03	-0.57	-1.51	-0.02	-0.02	-0.01
H	3	17.83	28.72	0.07	0.21	0.09	-0.37	-1.49	0.02	-0.01	-0.01
H	4	24.43	16.35	0.40	0.24	0.01	-1.39	-0.37	-0.01	-0.04	0.01
H	5	26.69	7.78	0.38	0.19	0.09	-1.14	-0.72	-0.06	-0.03	-0.01
H	6	25.66	9.54	0.50	0.19	0.08	-1.12	-0.48	-0.01	-0.03	-0.01
C	1	-2.82	-135.73	0.50	3.50	0.72	-4.16	2.28	0.01	-0.15	0.03
C	2	132.34	35.96	0.35	3.02	0.37	-6.04	-2.12	-0.05	-0.13	-0.04
N	1	191.45	13.23	0.25	1.27	0.14	-8.62	-0.12	0.13	-0.01	-0.02
O	1	-63.19	524.97	0.42	8.53	0.04	-13.93	-14.39	-0.01	-0.14	0.04
O	2	78.64	-242.91	0.12	-7.69	0.23	-11.92	0.19	-0.01	0.17	0.01
Cl	1	885.22	90.69	0.67	-8.14	0.80	-14.12	-1.85	0.00	0.43	0.01

Table S3. The calculated static NMR parameters and MD-induced changed of the parameters for α-glycine. The atom numbering is identical to that in the crystallographic database.

		σ_{iso} [ppm]	$\Delta\delta$ [ppm]	η	χ [MHz]	η_Q	$\Delta\sigma_{iso}$ [ppm]	$\Delta\Delta\delta$ [ppm]	$\Delta\eta$	$\Delta\chi$ [MHz]	$\Delta\eta_Q$
H	1	19.82	27.61	0.17	0.15	0.03	0.22	-1.56	-0.01	0.00	-0.01
H	2	22.40	22.10	0.05	0.18	0.04	-0.34	-0.89	0.00	-0.01	0.00
H	3	24.96	14.91	0.26	0.21	0.00	-0.85	-0.17	-0.02	-0.02	0.00
H	4	26.73	8.45	0.61	0.18	0.04	-0.76	-0.17	-0.04	-0.03	0.00
H	5	27.79	-4.61	0.99	0.19	0.09	-0.56	2.70	0.04	-0.02	-0.01
C	1	-4.97	107.45	0.99	3.51	0.00	-2.85	-0.59	-0.02	-0.12	0.04
C	2	130.49	33.26	0.79	3.09	0.26	-4.01	-2.05	-0.05	-0.10	-0.03
N	1	194.54	-14.07	0.63	1.31	0.54	-4.72	-0.01	0.01	0.02	-0.05
O	1	-35.56	372.31	0.65	7.21	0.45	-11.82	1.11	-0.03	0.00	0.01
O	2	-24.32	338.67	0.59	7.52	0.49	-11.72	-0.68	-0.02	-0.09	0.02

Table S4. The calculated static NMR parameters and MD-induced changed of the parameters for L-alanine. The atom numbering is identical to that in the crystallographic database.

		σ_{iso} [ppm]	$\Delta\delta$ [ppm]	η	χ [MHz]	η_Q	$\Delta\sigma_{iso}$ [ppm]	$\Delta\Delta\delta$ [ppm]	$\Delta\eta$	$\Delta\chi$ [MHz]	$\Delta\eta_Q$
H	1	24.08	20.72	0.11	0.20	0.06	-0.64	-0.89	0.01	-0.02	0.00
H	2	27.13	8.57	0.40	0.18	0.06	-0.25	-0.33	-0.03	0.00	-0.01
H	3	30.33	7.33	0.11	0.21	0.03	-0.66	-0.83	0.02	-0.03	0.02
H	4	20.50	26.77	0.18	0.16	0.02	0.06	-1.14	-0.01	0.00	-0.01
H	5	29.73	7.83	0.19	0.20	0.02	-0.58	-0.89	0.02	-0.03	0.01
H	6	22.90	22.77	0.12	0.19	0.04	-0.11	-1.09	0.00	-0.01	-0.01
H	7	30.05	6.33	0.20	0.21	0.03	-0.63	-0.83	-0.02	-0.03	-0.01
C	1	-6.62	106.45	0.89	3.51	0.09	-3.33	-1.00	0.01	-0.15	0.02
C	2	122.02	34.83	0.47	2.97	0.19	-2.54	-1.02	-0.06	-0.02	0.04
C	3	156.52	21.11	0.81	1.11	0.10	-4.48	-1.17	0.03	-0.06	0.01
N	1	185.98	-18.85	0.84	1.29	0.23	-4.75	9.68	0.04	0.00	0.00
O	1	-29.25	420.63	0.49	8.32	0.26	-13.29	-7.54	-0.02	-0.12	0.03
O	2	-11.91	311.82	0.65	6.81	0.65	-14.18	-0.03	-0.02	0.03	0.01

Table S5. The calculated static NMR parameters and MD-induced changed of the parameters for valine hydrochloride. The atom numbering is identical to that in the crystallographic database.

		σ_{iso} [ppm]	$\Delta\delta$ [ppm]	η	χ [MHz]	η_Q	$\Delta\sigma_{iso}$ [ppm]	$\Delta\Delta\delta$ [ppm]	$\Delta\eta$	$\Delta\chi$ [MHz]	$\Delta\eta_Q$
H	1	23.77	21.96	0.13	0.20	0.04	-0.61	-0.80	0.00	-0.02	0.00
H	2	30.02	10.45	0.63	0.22	0.04	-1.32	-1.31	0.02	-0.06	-0.01
H	3	31.42	7.90	0.30	0.22	0.03	-1.30	-1.27	0.01	-0.06	0.00
H	4	30.67	10.53	0.29	0.21	0.03	-1.22	-1.30	-0.03	-0.05	0.02
H	5	22.46	27.80	0.17	0.19	0.03	-0.32	-1.47	-0.01	-0.02	-0.01
H	6	30.34	9.09	0.47	0.21	0.03	-1.03	-1.12	-0.01	-0.05	0.02
H	7	30.49	8.62	0.29	0.21	0.03	-0.88	-0.86	-0.05	-0.04	0.00
H	8	30.28	7.12	0.58	0.21	0.04	-1.16	-1.02	-0.01	-0.06	0.01
H	9	23.05	22.11	0.25	0.20	0.01	-0.42	-1.29	0.00	-0.02	0.00
H	10	28.49	9.00	0.55	0.18	0.03	-0.72	-0.55	-0.06	-0.02	0.00
H	11	17.91	30.69	0.07	0.19	0.11	-0.12	-1.62	0.00	-0.02	-0.01
H	12	26.19	7.38	0.45	0.17	0.07	-0.34	-0.34	-0.01	-0.01	0.00
C	1	-0.90	-134.70	0.45	3.43	0.72	-5.21	1.84	0.00	-0.19	0.05
C	2	113.11	-24.61	0.71	3.04	0.32	-3.07	1.99	-0.18	-0.14	0.03
C	3	143.95	-17.61	0.86	1.13	0.62	-5.38	0.89	-0.17	-0.01	-0.04
C	4	162.28	27.29	0.29	0.72	0.20	-9.63	-0.82	-0.17	-0.12	0.06
C	5	157.14	30.96	0.53	0.83	0.20	-6.23	-1.43	0.08	-0.14	-0.09
N	1	182.10	-21.21	0.66	1.12	0.18	-5.88	0.86	0.06	-0.02	-0.03
O	1	-76.80	524.33	0.40	8.59	0.08	-19.35	-12.47	-0.01	-0.17	0.03
O	2	68.36	-235.46	0.15	-7.60	0.22	-14.64	-5.72	-0.03	0.15	0.02
Cl	1	890.83	115.47	0.88	-7.96	0.56	-16.01	-4.36	-0.04	0.33	-0.03

Table S6. The calculated static NMR parameters and MD-induced changed of the parameters for tyrosine hydrochloride. The atom numbering is identical to that in the crystallographic database.

		σ_{iso} [ppm]	$\Delta\delta$ [ppm]	η	χ [MHz]	η_Q	$\Delta\sigma_{iso}$ [ppm]	$\Delta\Delta\delta$ [ppm]	$\Delta\eta$	$\Delta\chi$ [MHz]	$\Delta\eta_Q$
H	1	24.26	21.29	0.11	0.24	0.01	-0.84	-1.77	0.00	-0.04	0.02
H	2	20.78	29.75	0.26	0.23	0.14	-0.15	-2.54	-0.02	-0.03	-0.02
H	3	26.59	10.90	0.52	0.19	0.04	-0.38	-0.98	0.00	-0.01	0.00
H	4	28.86	7.73	0.75	0.20	0.03	-0.63	-0.37	0.01	-0.02	-0.01
H	5	24.55	19.78	0.16	0.23	0.04	-1.41	-2.17	-0.01	-0.07	0.01
H	6	17.48	28.75	0.20	0.17	0.12	-0.10	-1.57	0.00	-0.01	0.00
H	7	25.73	5.44	0.14	0.21	0.06	-0.37	-0.11	-0.01	-0.01	0.00
H	8	23.49	-3.03	0.93	0.19	0.07	-0.29	-0.15	0.02	-0.01	-0.01
H	9	24.19	16.32	0.31	0.23	0.04	-2.25	-1.36	0.18	-0.08	-0.02
H	10	24.10	-3.94	0.55	0.19	0.07	-0.26	0.20	-0.01	-0.02	-0.02
H	11	25.78	3.19	0.41	0.20	0.07	-0.45	-0.27	0.00	-0.02	0.00
H	12	26.26	7.47	0.35	0.17	0.06	-0.64	-0.01	0.00	-0.02	0.00
C	1	-1.04	-139.17	0.47	3.41	0.64	-4.98	0.98	0.02	-0.10	0.03
C	2	114.00	20.99	0.51	3.16	0.21	-3.90	-1.87	0.00	-0.15	0.02
C	3	35.28	174.63	0.73	2.89	0.03	-2.67	-2.47	0.00	-0.10	-0.01
C	4	38.95	181.83	0.70	2.70	0.17	-2.77	-3.62	-0.01	-0.12	0.00
C	5	136.29	28.85	0.75	1.35	0.73	-4.82	-28.77	-0.01	-0.04	0.01
C	6	55.68	150.96	0.67	2.11	0.25	-2.47	-3.38	-0.01	-0.09	0.00
C	7	50.70	161.95	0.58	2.30	0.19	-3.63	-2.10	0.01	-0.08	0.00
C	8	15.51	131.32	0.95	-3.43	0.11	-2.15	-3.35	0.02	0.06	0.04
C	9	41.59	183.70	0.64	2.08	0.68	-2.90	-2.66	-0.02	-0.07	0.01
N	1	184.04	17.95	0.58	1.06	0.34	-12.99	0.08	-0.16	-0.03	-0.09
O	1	-59.18	522.49	0.29	8.40	0.02	-15.13	-10.01	-0.02	-0.03	0.06
O	2	73.35	-240.41	0.28	-7.37	0.19	-10.90	-1.55	0.01	0.06	0.00
O	3	168.15	-60.87	0.64	-8.82	0.82	-8.21	-2.97	0.03	0.10	-0.04
Cl	1	887.73	-83.56	0.50	-3.63	0.37	-22.71	16.85	0.27	-0.07	-0.17

Table S7. The calculated static NMR parameters and MD-induced changed of the parameters for glutamic acid hydrochloride. The atom numbering is identical to that in the crystallographic database.

		σ_{iso} [ppm]	$\Delta\delta$ [ppm]	η	χ [MHz]	η_Q	$\Delta\sigma_{iso}$ [ppm]	$\Delta\Delta\delta$ [ppm]	$\Delta\eta$	$\Delta\chi$ [MHz]	$\Delta\eta_Q$
H	1	17.10	23.47	0.17	0.17	0.13	0.23	-1.91	0.01	-0.01	-0.01
H	2	27.70	6.31	0.91	0.17	0.06	-0.88	-0.89	-0.06	-0.04	-0.02
H	3	18.65	27.52	0.11	0.24	0.09	0.14	-1.97	0.00	-0.01	-0.01
H	4	23.86	18.06	0.32	0.20	0.02	-0.57	-0.85	-0.01	-0.02	-0.01
H	5	20.87	29.12	0.15	0.16	0.04	-0.26	-1.45	-0.01	-0.02	-0.01
H	6	20.73	27.36	0.12	0.13	0.06	-0.57	-0.84	-0.01	-0.02	-0.01
H	7	27.25	6.65	0.76	0.19	0.05	-0.61	-0.22	0.02	-0.02	0.00
H	8	28.52	7.95	0.37	0.20	0.05	-1.12	-0.92	-0.09	-0.04	-0.03
H	9	29.63	6.57	0.33	0.22	0.04	-1.09	-0.67	-0.02	-0.04	-0.03
H	10	28.08	5.99	0.45	0.18	0.05	-1.11	-0.92	0.16	-0.04	-0.03
C	1	-8.18	-128.15	0.70	3.50	0.57	-4.90	0.03	-0.02	-0.18	0.05
C	2	117.94	26.30	0.70	2.75	0.41	-3.53	-1.81	0.07	-0.11	0.00
C	3	145.85	25.67	0.48	1.40	0.86	-6.24	-2.59	0.01	-0.15	0.02
C	4	141.98	30.91	0.44	0.65	0.59	-6.37	-1.61	0.01	-0.10	0.02
C	5	-8.15	-120.44	0.83	3.72	0.81	-5.43	-0.99	-0.05	-0.20	0.05
N	1	179.50	-6.85	0.76	1.21	0.14	-6.20	0.11	-0.22	0.00	-0.03
O	1	79.70	-242.07	0.33	-7.41	0.24	-10.66	-2.51	-0.03	0.08	0.00
O	2	-58.68	500.48	0.33	8.40	0.09	-18.88	-8.99	-0.01	0.00	0.05
O	3	-56.63	468.19	0.34	8.69	0.20	-15.44	-12.21	-0.01	-0.18	0.04
O	4	70.63	-245.86	0.10	-8.13	0.13	-12.10	-3.00	-0.04	0.22	0.06
Cl	1	876.38	68.75	0.66	4.33	0.30	-19.76	58.99	0.16	-0.44	-0.06

Table S8. The calculated static NMR parameters and MD-induced changed of the parameters for phenylalanine hydrochloride. The atom numbering is identical to that in the crystallographic database.

		σ_{iso} [ppm]	$\Delta\delta$ [ppm]	η	χ [MHz]	η_Q	$\Delta\sigma_{iso}$ [ppm]	$\Delta\Delta\delta$ [ppm]	$\Delta\eta$	$\Delta\chi$ [MHz]	$\Delta\eta_Q$
H	1	23.27	22.07	0.14	0.16	0.04	-0.75	-1.01	0.02	-0.03	0.00
H	2	22.92	28.50	0.15	0.20	0.03	-0.46	-1.54	-0.01	-0.02	-0.01
H	3	28.07	5.32	0.32	0.20	0.03	-0.59	-0.53	0.04	-0.03	-0.01
H	4	28.43	9.57	0.46	0.18	0.03	-0.69	-0.37	-0.01	-0.02	-0.02
H	5	25.36	20.32	0.29	0.27	0.01	-0.92	-0.82	-0.03	-0.03	0.01
H	6	24.08	5.52	0.30	0.27	0.05	-0.43	-0.12	-0.11	-0.03	-0.01
H	7	23.71	2.53	0.36	0.22	0.06	-0.45	-0.08	0.15	-0.02	-0.01
H	8	18.51	28.24	0.11	0.20	0.10	-0.18	-2.06	-0.01	-0.02	-0.01
H	9	25.73	7.64	0.39	0.25	0.05	-0.61	-0.50	0.01	-0.02	-0.01
H	10	23.70	2.40	0.75	0.30	0.04	-0.49	0.05	0.00	-0.03	-0.01
H	11	23.90	-2.11	0.38	0.24	0.05	-0.40	0.00	0.16	-0.03	0.00
H	12	25.86	7.50	0.30	0.17	0.07	-0.39	-0.40	-0.01	-0.01	0.00
C	1	-0.82	-134.42	0.46	3.44	0.75	-7.42	1.15	0.03	-0.21	0.04
C	2	116.14	32.61	0.74	2.97	0.36	-2.84	-1.99	-0.01	-0.11	0.00
C	3	139.49	17.24	0.25	1.15	0.81	-4.59	-0.71	0.10	-0.06	0.06
C	4	33.09	201.90	0.55	2.66	0.43	-3.89	-6.72	0.01	-0.22	-0.01
C	5	41.58	185.95	0.80	2.92	0.10	-4.85	-7.41	-0.01	-0.20	0.04
C	6	35.95	191.28	0.69	2.99	0.02	-4.26	-5.89	0.00	-0.22	0.01
C	7	39.94	206.39	0.63	3.16	0.05	-4.79	-7.60	0.00	-0.25	-0.03
C	8	40.54	201.22	0.72	3.08	0.10	-4.74	-10.13	0.00	-0.24	0.06
C	9	39.32	204.02	0.70	2.98	0.05	-4.28	-8.95	0.01	-0.27	-0.02
N	1	187.99	14.25	0.60	1.17	0.29	-7.98	9.68	-0.03	0.03	-0.04
O	1	-77.96	542.24	0.39	8.62	0.10	-25.33	-13.67	-0.02	0.03	0.05
O	2	73.35	-250.48	0.23	-7.79	0.22	-16.47	-2.72	0.00	0.22	-0.02
Cl	1	890.36	114.68	0.84	-7.71	0.55	-18.82	-4.93	-0.05	0.04	-0.04

Table S9. The calculated static NMR parameters and MD-induced changed of the parameters for cytosine. The atom numbering is identical to that in the crystallographic database.

		σ_{iso} [ppm]	$\Delta\delta$ [ppm]	η	χ [MHz]	η_Q	$\Delta\sigma_{iso}$ [ppm]	$\Delta\Delta\delta$ [ppm]	$\Delta\eta$	$\Delta\chi$ [MHz]	$\Delta\eta_Q$
H	1	17.07	19.88	0.30	0.14	0.25	-0.08	-1.19	-0.01	-0.01	-0.01
H	2	22.66	15.78	0.18	0.20	0.18	-0.13	-1.11	-0.01	-0.02	-0.02
H	3	23.52	16.66	0.34	0.21	0.18	-0.28	-1.11	-0.01	-0.02	-0.02
H	4	25.69	2.55	0.69	0.20	0.08	-0.43	-1.21	0.04	-0.02	-0.01
H	5	23.58	-2.22	0.53	0.19	0.05	-0.36	-0.11	-0.06	-0.01	-0.01
C	1	12.90	-104.60	0.90	2.46	0.72	-2.65	0.99	-0.01	-0.09	0.03
C	2	5.87	162.46	0.29	3.18	0.42	-2.68	-2.32	0.02	-0.11	0.01
C	3	79.99	126.64	0.96	1.35	0.70	-3.51	-2.53	-0.01	-0.09	0.01
C	4	26.06	171.47	0.79	3.09	0.98	-3.06	-2.72	-0.02	-0.09	0.02
N	1	68.52	170.70	0.55	-2.14	0.77	-7.44	0.70	0.02	0.04	0.03
N	2	13.51	253.27	0.49	-2.85	0.79	-6.29	-2.10	0.00	0.05	0.03
N	3	127.50	-104.77	0.13	-3.23	0.32	-4.58	2.51	0.00	0.08	0.01
O	1	27.11	327.11	0.16	7.72	0.66	-11.34	-6.53	0.01	-0.08	0.00

Table S10. The calculated static NMR parameters and MD-induced changed of the parameters for thymine. The atom numbering is identical to that in the crystallographic database.

		σ_{iso} [ppm]	$\Delta\delta$ [ppm]	η	χ [MHz]	η_Q	$\Delta\sigma_{iso}$ [ppm]	$\Delta\Delta\delta$ [ppm]	$\Delta\eta$	$\Delta\chi$ [MHz]	$\Delta\eta_Q$
H	1	19.04	17.66	0.16	0.18	0.20	-0.12	-1.11	-0.02	-0.01	-0.01
H	2	18.62	15.66	0.06	0.18	0.18	-0.13	-0.77	0.01	-0.01	-0.01
H	3	23.37	4.23	0.55	0.18	0.08	-0.17	-0.27	-0.01	-0.01	-0.01
H	4	29.77	8.49	0.43	0.19	0.03	-0.04	-3.50	0.23	-0.11	0.55
H	5	29.27	7.25	0.58	0.19	0.03	-0.59	-7.72	0.17	-0.13	0.65
H	6	29.52	8.39	0.20	0.19	0.02	-0.26	-9.20	0.18	-0.16	0.66
C	1	14.86	94.83	0.87	2.25	0.41	-2.26	-0.53	0.02	-0.06	-0.01
C	2	7.33	-134.62	0.63	2.90	1.00	-2.33	0.29	-0.03	1.47	-0.02
C	3	53.65	144.34	0.63	1.65	0.65	-1.75	-3.90	0.03	-0.11	0.06
C	4	30.83	-152.09	0.88	-3.14	0.52	-2.61	1.88	0.01	0.10	-0.02
C	5	157.48	20.91	0.49	0.91	0.35	-1.18	-0.83	0.05	0.04	0.07
N	1	86.86	-132.77	0.99	-2.78	0.53	-5.38	-68.77	0.00	0.01	0.00
N	2	58.20	-118.20	0.82	-2.67	0.49	-4.99	-0.65	0.00	0.03	0.02
O	1	57.37	289.81	0.21	6.96	1.00	-13.07	-4.83	0.00	0.07	0.02
O	2	-70.12	582.08	0.52	9.08	0.14	-13.01	-8.12	-0.01	-0.12	0.01

References

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