

Supporting Information: High-pressure crystal structure of methyl iodide: molecular aggregation in the crystals of halomethanes and their isostructural relations

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H-atoms location

The location of H-atoms from X-ray data, and particularly for high-pressure measurements, is often doubtful. Therefore we have considered several models in our investigation, including the ordered and disordered ones. The inspection of the neutron-diffraction study at 4.5 K (R. M. Ibberson and M. Prager, *Z. Kristallogr.*, 2007, **222**, 416) showed that at this very low temperature the protons are markedly smeared around the carbon, indicating that there is a considerable freedom for their rotation and no severe barriers exist to stop it. This is consistent with the general knowledge on the behaviour of methyls in molecules, and in CH₃I the methyl rotations are dumped by intermolecular interactions only. The comparison of the ordered and disordered models showed that the disorder gave a marginally better fit even at the presence of the heavy iodine atom. Moreover, we could see that the disordered sites approached systematically with increased pressure. Therefore this disordered model has been chosen for the final structural refinements. The two sets of disordered methyl H-atoms order with increasing pressure at the orientation corresponding to the shortest intermolecular C–H $\cdots$ I distances (see Figure S2). The narrowing distance between pairs of disordered H-atoms is: 0.72 Å at 0.53 GPa, 0.64 Å at 1.16 GPa, and 0.35 Å at 2.53 GPa. The narrowing of the distance between the disordered H-sites is consistent with the general knowledge about the influence of pressure, which should gradually eliminate disorder, as the H $\cdots$ I distances decrease. The I-atoms push the H atoms into the space, which is consistent with the H-sites determined by neutron diffraction at 4.5 K (Fig. S2).

It should be stressed, that the high-pressure results are affected by several effects that were corrected as precisely as possible, and that the H-atoms coordinates have been obtained from free refinement (except for the AFIX 137 constrain).

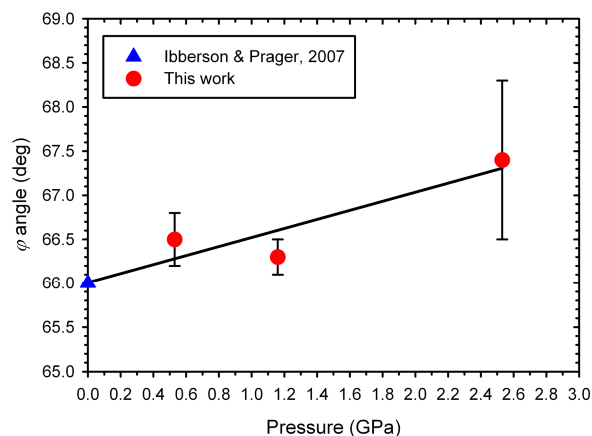


Figure S1. The pressure (GPa) dependence of the ϕ angle ($^{\circ}$). The blue triangle represent the data after R. M. Ibberson and M. Prager, *Z. Kristallogr.*, 2007, **222**, 416, from the CD_3I structure measured at 0.1 MPa/4.5 K, while the red circles represent our data from the CH_3I structures measured at 0.53, 1.16 and 2.53 GPa (all at 295 K).

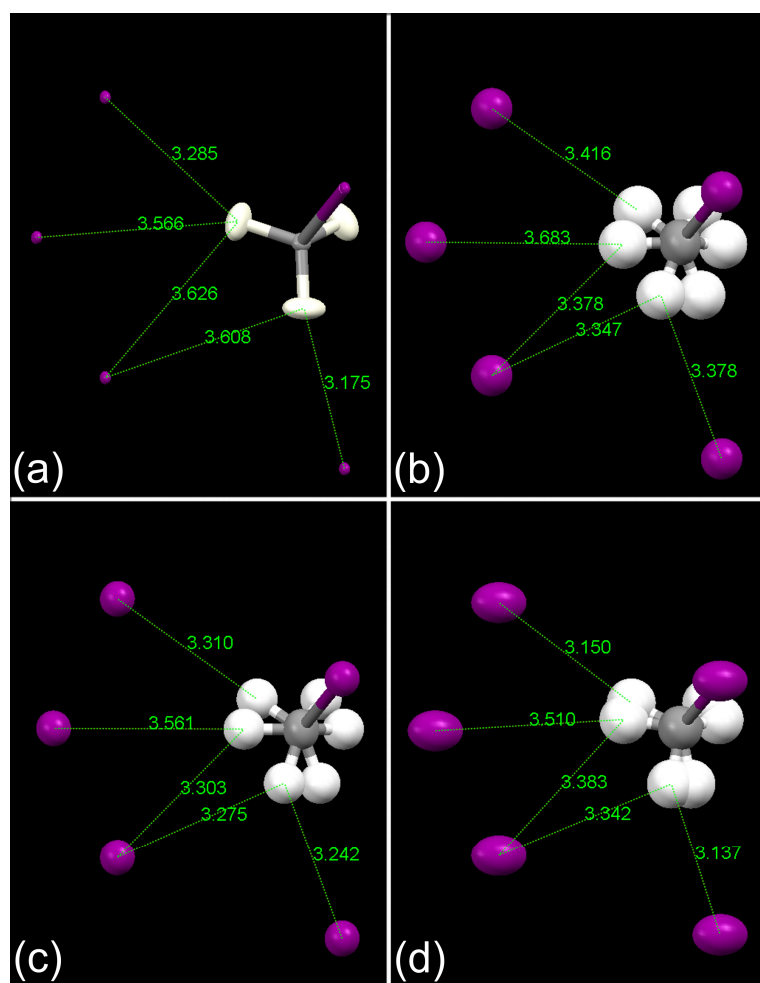


Figure S2. The CH_3I crystal-structure models refined for the diffraction data measured at: (a) 0.1 MPa/4.5 K; (b) 0.53 GPa/295 K; (c) 1.16 GPa/295 K and (d) 2.53 GPa/295 K. The hydrogen atoms have been refined with the AFIX 137 constrain of SHELXL (G. M.

Sheldrick, 1997, *SHELXS-97* and *SHELXL-97*, University of Göttingen), as explained above.
The shortest intermolecular H...I distances have been indicated.

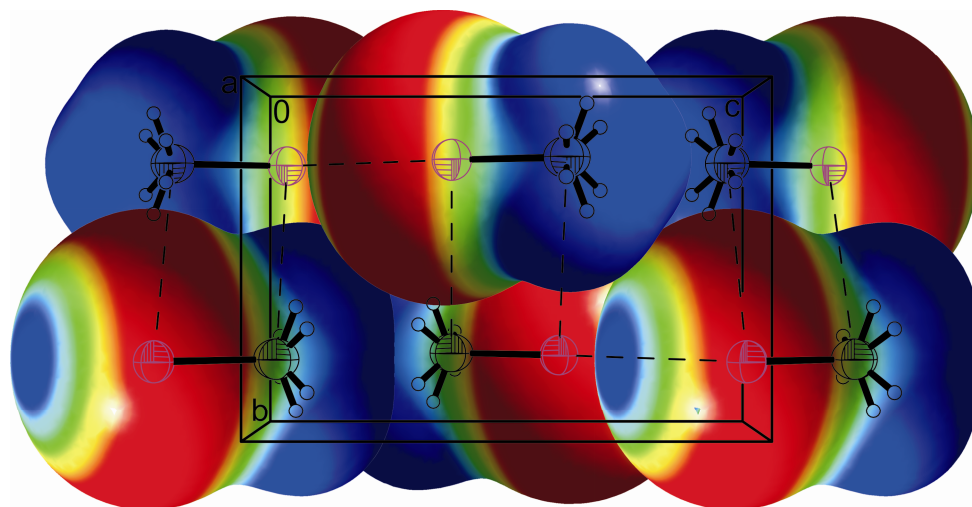


Figure S3. Molecular arrangement of CH₃I structure determined at 1.16 GPa/295 K viewed along *a*.

Table S1. Atomic coordinates ($\cdot 10^4$), U_{eq} for CH₃I at 0.53, 1.16 and 2.53 GPa. The H-atom positions are listed in the CIF's.

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	U_{eq}/U_{iso}
0.53 GPa/295 K				
I1	1560(1)	2500	946(1)	51(1)
C1	3448(20)	2500	−1018(9)	60(3)
1.16 GPa/295 K				
I1	1544(1)	2500	948(1)	36(1)
C1	3500(16)	2500	−1046(8)	43(2)
2.53 GPa/295 K				
I1	1552(3)	2500	949(1)	65(4)
C1	3377(72)	2500	−997(22)	60(8)

Table S2. Selected interatomic distances (Å) and angles (°) of crystalline CH₃I structure in high pressure compared with those observed in low-temperature. The φ angle is the angle between the C–I bond and the [100] direction (see Figure 4).

CH ₃ I at:	0.1 MPa/193 K ^a	0.1 MPa/4.5 K ^b	0.53 GPa/295 K ^c	1.16 GPa/295 K ^c	2.53 GPa/295 K ^c
molecular dimensions					
C1–I1 (Å)	2.130(60)	2.146(1)	2.129(9)	2.127(7)	2.026(20)
C1–H1 (Å)	–	1.078(1)	0.96	0.96	0.96
intermolecular dimensions					
I1...I1 ⁱ (Å)	3.895(10)	3.835(1)	3.8204(10)	3.7375(9)	3.6666(25)
∠C1–I1...I1 ⁱ (°)	164(2)	167.73	167.45(25)	167.94(19)	167.02(89)
∠I1...I1 ⁱ –C1 ⁱ (°)	124(2)	119.76	120.44(25)	120.62(19)	121.80(89)
I1...I1 ^j (Å)	4.25	4.168	4.1485(8)	4.0510(7)	3.9845(44)
∠C1–I1...I1 ^j (°)	72	74.72	73.68(13)	73.42(10)	72.86(45)
∠I1...I1 ^j –C1 ^j (°)	72	74.72	73.68(13)	73.42(10)	72.86(45)
H1...I1 ^k (Å)	–	3.175	3.378	3.242	3.137
C1...I1 ^k (Å)	4.363	4.155	4.137(9)	4.015(7)	3.958(31)
H1...I1 ^l (Å)	–	3.285	3.416	3.310	3.150
C1...I1 ^l (Å)	4.112	4.155	4.096(5)	4.002(4)	3.902(17)
H1...I1 ^m (Å)	–	3.566	3.683	3.561	3.510
C1...I1 ^m (Å)	4.640	4.548	4.562(6)	4.449(5)	4.406(15)
H1...I1 ⁿ (Å)	–	3.608	3.347	3.275	3.342
C1...I1 ⁿ (Å)	4.256	4.069	4.092(5)	3.982(4)	3.935(17)
H1...I1 ^o (Å)	–	3.626	3.378	3.303	3.383
C1...I1 ^o (Å)	4.256	4.069	4.092(5)	3.982(4)	3.935(17)
∠ φ (°)	70.2	66	66.5(3)	66.3(2)	67.4(9)

^a T. Kawaguchi, M. Hijikigawa, Y. Hayafuji, M. Ikeda, R. Fukushima and Y. Tomiie, *Bull. Chem. Soc. Jpn.*, 1973, **46**, 53;

^b R. M. Ibberson and M. Prager, *Z. Kristallogr.*, 2007, **222**, 416 (low-temperature structure of CD₃I);

^c This work;

Symmetry codes: (i) $-0.5+x, y, 0.5-z$; $0.5+x, y, 0.5-z$; (j) $-x, -y, -z$; $-x, 1-y, -z$; (k) $1+x, y, z$; (l) $-x, 1-y, -z$; (m) $0.5-x, -y, -0.5+z$; (n) $1-x, 1-y, -z$; (o) $1-x, -y, -z$.