

# 1 **Prospects for mineralogy on Titan (revision 1)**

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## 8 **Abstract**

9 Saturn's moon Titan has a surface that is dominated by molecular materials, much of  
10 which is photochemically produced in the moon's atmosphere. This outlook reviews  
11 the potential minerals that would be expected to form on the surface and subsurface of  
12 Titan from these molecular solids. We seek to classify them and look towards how  
13 the future study of these minerals will enhance our understanding of this planetary  
14 body. The classification uses the basis of intermolecular interactions, with the  
15 materials grouped into 'Molecular solids', 'Molecular co-crystals' and 'Hydrates'  
16 classes alongside speculation on other possible classes of potential Titan minerals.

## 17 **Introduction**

18 The Cassini-Huygens mission has revealed Saturn's largest moon Titan to be a  
19 diverse world, with geological features that are astonishingly similar to those found  
20 on our own world. With vast seas and lakes, sweeping dunes and dendritic channels,  
21 the evidence is mounting that the landscape of Titan has been shaped by both fluvial  
22 and pluvial processes. However, there are stark differences between Earth and Titan,  
23 such as the temperatures and materials that shape their respective landscapes, Fig. 1.

24 Unlike the vast temperature variability we experience on Earth, Titan has a surface  
25 temperature that has hardly been observed to vary from 92 K (Cottini et al., 2012).  
26 Additionally, Earth's surface is made up of minerals that are largely silicate or metal-  
27 based, with their structures and physical properties well established over the last  
28 century. This is in contrast to Titan, where the bulk density of this body of  $1.88 \text{ gcm}^{-3}$   
29 (Jacobson et al., 2006) points to the surface and subsurface being composed of simple  
30 molecular materials such as water ice, ammonia and organic materials such as  
31 hydrocarbons and nitriles accompanied by hydrocarbon liquids (Stevenson, 1992).  
32 Additionally, accumulation and redistribution of molecular materials produced photo-  
33 chemically in the moon's atmosphere also shape the surface we observe (Lorenz et  
34 al., 2008) (Janssen et al., 2009).

35 ~Fig. 1 here~

36 Photochemical processes in Titan's atmosphere are driven by solar radiation and  
37 energy from Saturn's magnetosphere. These processes cause nitrogen and methane to  
38 dissociate into radicals and then recombine, generating organic molecules that range  
39 from simple (ethane, acetylene and hydrogen cyanide) to complex molecules (Cable  
40 et al., 2011) (Carrasco et al., 2009) (He and Smith, 2014) (Pernot et al., 2010)  
41 (Sciamma-O'Brien et al., 2014). The more complex molecules formed by these  
42 processes would first form as haze layers in Titan's atmosphere, and continue to react  
43 and grow before being deposited on the surface. A range of photochemical models  
44 have been used to assess the molecular species and flux of these upon Titan's surface  
45 (such as (Lavvas et al., 2008) (Krasnopolsky, 2009) (Krasnopolsky, 2014) (Cordier et  
46 al., 2009) and (Willacy et al., 2016)), which are summarised in Table 1.

47 ~Table 1 here ~

48 This information leads us to wonder, what are the molecular minerals that shape the  
49 surface of Titan? What crystal structures control the surface processes on this frozen  
50 world? This is not without precedent here on Earth, where the International  
51 Mineralogical Association recognises approximately 50 mineral species that  
52 incorporate organic molecules (Hazen et al., 2013). There exists a number of types of  
53 these materials too; from the mineral karpaitite, predominately formed of the molecule  
54 coronene (C<sub>24</sub>H<sub>12</sub>) (Echigo et al., 2007), to minerals with metal organic framework  
55 structures (Huskić et al., 2016) as well as one example of a geoporphyrin (Hummer et  
56 al., 2017).

57 There has, to date, been a number of contributions that have discussed Titan's  
58 geological processes with references to the minerals that possibly govern them. This  
59 has included erosion (Lorenz and Lunine, 1996), possible cryovolcanism (Fortes et  
60 al., 2007) and the sequence of evaporite mineral formation (Malaska et al., 2012).  
61 However these have largely concentrated on selected materials, subsets of the array of  
62 molecules that are thought to exist on Titan's surface. Hence, we have viewed it as  
63 timely to conduct a survey of known solid phases from the organic molecules that are  
64 predicted to be present on Saturn's largest moon.

### 65 **Survey of the Cambridge Structural Database**

66 We have surveyed the current understanding of molecular solids formed from the  
67 species outlined in Table 1 using the Cambridge Structural Database (CSD) version  
68 5.37 (Groom et al., 2016). This information has been used to discern the possible  
69 mineral 'types' that would be expected on the surface of Titan. Administered by the  
70 Cambridge Crystallographic Data Centre (CCDC), the CSD is the foremost repository  
71 of organic molecular crystal structures, containing 800,000 deposited structures.

72 Hence, it is an ideal database to undertake a survey of organic solids that could form  
73 at the cryogenic temperatures of Titan. Using the CCDC's Conquest (Bruno et al.,  
74 2002) program, a search for each molecular species was undertaken, with the results  
75 summarised in Table 2.

76 ~ Table 2 here ~

77 In the remainder of this article, we outline the current knowledge on these materials in  
78 the context of Titan's surface and subsurface, and speculate on the potential of these  
79 to template and provide surfaces for catalytic activity.

## 80 **Molecular solids**

81 Many of the molecules listed in Table 1, could exist on the surface of Titan in their  
82 pure solid states. Fig. 2 presents three of the crystal structures of species listed in  
83 Table 1, and illustrates the variety of inter-molecular bonding these materials exhibit,  
84 including C-H... $\pi$  interactions (for acetylene), London forces (propane) and C-  
85 H...N $\equiv$ C interactions (acetonitrile). Additionally, many of these molecular solids  
86 form crystal structures where the molecules exhibit positional disorder, which can  
87 range from affecting just part of the molecule to the whole molecule being  
88 rotationally disordered.

89 ~ Fig. 2 here ~

90

91 It is this tendency for positionally disordered crystal structures that give this class of  
92 Titan materials their potential to shape the surface, since at Titan's low temperatures  
93 many of these molecular solids undergo phase transformations where the molecules  
94 become partially or fully ordered. This change to ordered crystal structures often has  
95 a number of effects, most noticeably an increase in density, often quite significant.

96 For instance the change between cubic and monoclinic ethane increases the density by  
97 7 % (van Nes and Vos, 1978). The species outlined in Table 1 that undergo phase  
98 transitions with temperature, driven by the ordering of their molecules are: ethane  
99 (cubic to monoclinic at 88 K), acetylene (cubic to orthorhombic at 133 K (McMullan  
100 et al., 1992)), HCN (tetragonal to orthorhombic at 170 K (Dulmage and Lipscomb,  
101 1951)) and acetonitrile (monoclinic to orthorhombic at 203 K - plus a possible lower  
102 temperature transition (Enjalbert and Galy, 2002)). Though the surface temperature  
103 of Titan varies very little from 92 K (Cottini et al., 2012) any burial of these  
104 molecular materials could reach temperatures that exceed each of the phase  
105 transformations listed. Any change in temperature would have also have a dramatic  
106 effect upon the low-temperature orthorhombic form of HCN, which is pyroelectric  
107 (Dulmage and Lipscomb, 1951) and could be a source of energy for further chemical  
108 reactions.

109 Differences in density can drive a number of geological processes, but additionally,  
110 some of these molecular solids (*n*-butane for instance) would form what is termed  
111 ‘plastic solids’ – any application of force would deform these materials in a non-  
112 reversible way. Therefore, understanding the formation and weathering of Titan  
113 materials may involve significant effort in characterising the evolution of  
114 microstructure at low temperatures, something that is rarely attempted experimentally.

### 115 **Molecular co-crystals**

116 As the Cassini-Huygens mission has shown, Titan is a world with an active weather,  
117 hydrologic (we use the term to include non-aqueous volatiles see (Barnes et al.,  
118 2011)) and sediment transport cycle, and it is likely that the molecular solids  
119 deposited on the surface of this moon will undergo physical and chemical processing.

120 This could occur by burial by subsequent layers of organic material or dissolution in  
121 the liquid hydrocarbon seas (Raulin, 1987) (Cordier et al., 2009) (Malaska and  
122 Hodyss, 2014) (Cordier et al., 2013). As has been proposed before (Glein and Shock,  
123 2013), such processes would lead to mixing of the pure molecular species outlined in  
124 the previous section, leading to the potential formation of more complex materials.  
125 These solid molecular materials would be composed of mixtures of multiple species  
126 listed in Table 1, but with a fixed stoichiometry: molecular co-crystals.

127 The chemical community usually excludes materials that include water molecules  
128 from their definitions of molecular co-crystals (these are more often referred to as  
129 hydrates or solvates). To date molecular co-crystals have been investigated with a  
130 number of aims, ranging from addressing the delivery of pharmaceutical molecules  
131 (Duggirala et al., 2016) to the control of energetic materials (Millar et al., 2012). As  
132 detailed in the Table 2, there are already a number of co-crystals known between  
133 potential Titan molecules and two are presented in Fig. 3. Notable in this, is the work  
134 of Kirchner and co-workers who investigated co-crystals of acetylene in a bid to  
135 explore weak interatomic potentials,  $\sim 5\text{-}20 \text{ kJ mol}^{-1}$  (Kirchner et al., 2010). This aim  
136 is particularly pertinent for the study of Titan minerals since, at 92 K, it is this range  
137 of inter-molecular interactions that could be modified in small variations of low-  
138 temperature conditions.

139 ~Fig. 2 here ~

140 Investigations into molecular co-crystals that would exist on Titan was taken up in  
141 earnest more recently, motivated by the aim of finding materials that make up Titan's  
142 evaporite deposits (MacKenzie et al., 2014) (Cordier et al., 2016). Raman spectra (Vu  
143 et al., 2014) and subsequent kinetic studies (Cable et al., 2014) revealed the existence

144 of a co-crystal between benzene and ethane. Diffraction studies showed this to be a  
145 novel material, with a two-dimensional host-guest structure where the benzene forms  
146 a host framework connected by intermolecular C-H... $\pi$  interactions and ethane a  
147 guest in the channels that form (Maynard-Casely et al., 2016). The discovery of this  
148 co-crystal has ignited study in this area, with potential acetylene:benzene and  
149 acetylene:ammonia co-crystals being subsequently identified (Cable, in preparation).  
150 The latter, in particular, has been shown to be more thermodynamically stable than  
151 the solids of pure ammonia or acetylene (Preston and Signorell, 2012), and is resistant  
152 to potential pluvial or fluvial weathering by liquid methane or ethane.

153 It has already been demonstrated that the 3:1 benzene:ethane co-crystal has greater  
154 expansive properties than other species thought to exist on the surface of Titan  
155 (Maynard-Casely et al., 2016). In the case of this material, this is attributed to the C-  
156 H... $\pi$  interactions, that can vary significantly in this temperature range. Hence, this  
157 group of potential Titan minerals, molecular co-crystals, would be characterised by  
158 dispersive, dipole and C-H... $\pi$  intermolecular interactions. The lower strength of  
159 these interactions, compared to other materials, would mean that these mineral phases  
160 would be more subjected to modification at 92 K than materials governed by stronger  
161 intermolecular interactions.

162 As listed in Table 2, very few non-binary molecular co-crystals with these species  
163 have been identified to date. There is a large scope for tertiary or even further multi-  
164 species co-crystals, a pursuit that warrants further investigation.

## 165 **Hydrates**

166 Any interaction between the photo-chemically produced molecules and the underlying  
167 water ice layers of Titan would have the potential to form hydrated materials. For a

168 more detailed review of current knowledge of physical properties and phase  
169 behaviour of hydrates applied to icy worlds the reader is directed to (Fortes and  
170 Choukroun, 2010). There are two groups of hydrates regularly proposed to be formed  
171 on Titan, gas clathrate hydrates (hereafter clathrates) and ammonia hydrates. Some of  
172 these materials, like methane or CO<sub>2</sub> clathrate, would be the strongest of the surface  
173 materials on Titan – even stronger than water ice (Durham et al., 2010). Ammonia  
174 hydrates would likely originate from primordial materials from the deep subsurface  
175 ocean crystallized within the crust (e.g. (Lunine et al., 2009) and therein), and it is  
176 unclear whether they would be expressed on the surface.

177 Clathrates have been hypothesised to exist on the surface of Titan for some time  
178 (Miller, 1961) where additional pressure and cold temperatures provided by the  
179 atmosphere of Titan and ready availability of gas species favours the production of  
180 these materials. As shown in Fig. 3, gas hydrates undertake clathrate host-guest  
181 structures, with the water molecules forming the host three-dimensional framework,  
182 and a variety of gas species (such as methane, ethane, acetylene and propane) sitting  
183 within this framework as the guest molecules.

184 ~Fig. 4 here ~

185 Clathrates could have formed early in Titan's history (Tobie et al., 2006) (Lunine et  
186 al., 2009), or they may also form from interaction at the surface between liquid  
187 hydrocarbons produced by photochemistry and the icy bedrock (Choukroun and  
188 Sotin, 2012). Whatever their origin, they have long been anticipated to play an  
189 important role in the storage of methane and be involved in the replenishment of this  
190 constituent to the atmosphere, via possible cryovolcanism (Lunine and Stevenson,



191 1987) (Choukroun et al., 2010) or substitution within the subsurface by other  
192 clathrate-forming molecules like ethane and propane (Choukroun and Sotin, 2012).  
193 Of particular relevance, given mounting evidence that these hydrate phases could  
194 exist below layers of molecular co-crystals, is their high pressure behaviors. To date,  
195 the relevance of ammonia hydrates to the evolution of Titan have centred about the  
196 instability at high pressures of the dihydrate form (Loveday et al., 2009). The fact  
197 that these structures are held together by a higher density of hydrogen bonds would  
198 intrinsically make ammonia hydrates stronger than clathrates, as suggested by the  
199 higher strength of hydrated sulfates (Durham et al., 2010), which also have a high  
200 density of hydrogen bonds.

#### 201 **Further classes of potential Titan minerals**

202 We have described three possible categories of Titan minerals, but in this outlook we  
203 wish to speculate that there may be further classes to consider. This speculation is  
204 driven by the fact that photochemical reactions in the Titan atmosphere are thought to  
205 form clusters of complex organic molecules, referred to as tholins (Cable et al., 2011).  
206 Any deposition of molecular heterogeneous tholins on the surface of Titan, via the  
207 thick haze that is observed, would increase the possibility for rich mineralogy on  
208 Titan. Such mixing could introduce the possibility of materials forming with  
209 substitutional disorder. Additionally, like many of the mineral systems on Earth,  
210 some of Titan's material systems could exist as solid solutions, as has been recently  
211 observed between CO<sub>2</sub> and N<sub>2</sub>O (Connor et al., 2017).

#### 212 **Conclusions and future studies.**

213 In classifying the possible minerals of Saturn's moon Titan, we hope to have shown  
214 where current understanding of these materials is, and where it has to go to be useful  
215 for future understanding of this icy moon. However, it is noted that the survey here  
216 has been restricted to a very limited set of elements; hydrogen, carbon, nitrogen and  
217 oxygen. Trace inclusion of other elements, provided for instance from meteoritic  
218 bombardment, could drive further structural variability. Additionally, though a  
219 number of polymorphs have already been identified across all of the classes we have  
220 described, this aspect remains largely unexplored for possible Titan minerals.

221 The classification has identified a large range of physical properties that would be  
222 expected in Titan minerals. Given that intermolecular forces have a great impact on  
223 the bulk strength of a material, it can be broadly stated that the molecular materials  
224 would be the weakest of the Titan materials, as strength will be determined by  
225 dispersion and dipole-dipole intermolecular interactions ( $\sim 3\text{-}20\text{ kJmol}^{-1}$ ). These  
226 would be followed in resilience by the molecular co-crystals, and then by the hydrate  
227 materials (gas hydrates, ammonia hydrates and water-ice) where the hydrogen bond  
228 ( $\sim 20\text{-}30\text{ kJmol}^{-1}$ ) would be the defining interaction. The molecular solids and  
229 molecular co-crystals will have very different (and currently unexplored) mechanical  
230 properties, with possibilities in some of the molecular solids for plastic deformation of  
231 surface species. Additionally, the contrast in physical and mechanical properties  
232 between these materials could drive the erosion and propagation of cracks that, in  
233 turn, would form the process for a diversity of surface features on Titan such as those  
234 observed by Cassini.

235 Intriguingly, a number of the molecular co-crystals (and intrinsically the gas hydrates)  
236 form clathrate or inclusion compounds, a feature that could create chemical gradients  
237 across the Titan surface. For instance, the host-guest structure of the benzene:ethane

238 co-crystal also raises the possibility that other molecules could substitute for the  
239 ethane in the structure, leading to a variability of mineralogy and a non-stoichiometric  
240 structure. The variety of inclusion compounds that have been identified as possible  
241 Titan minerals suggests that chemical gradients are likely to form. This raises the  
242 potential for astrobiological activity on Titan, since life tends to require a chemical or  
243 energy gradient to exploit.

#### 244 **Acknowledgments**

245 The authors acknowledge ideas and advice from the participants in the “Don't Follow  
246 (Just) the Water: Does Life Occur in Non-Aqueous Media?” workshop organized by  
247 the W.M. Keck Institute for Space Studies as well as Prof Hazen for his review of the  
248 article. RH, MC, MM and TV gratefully acknowledge support from NASA's Solar  
249 System Workings program. Part of this work has been conducted at the Jet Propulsion  
250 Laboratory, California Institute of Technology, under contract to NASA. Government  
251 sponsorship acknowledged. Crystal structure visualizations were drawn with the  
252 Mercury 3.7 program (Macrae et al., 2008).

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405

406

407 Table 1 – List of selected molecular species expected on the surface according to three  
 408 photochemical models as well as the implied flux of each molecule incident upon the Titan  
 409 surface. Those molecules where the specific model has not given a flux are denoted 'not  
 410 applicable' (N/A).

Species	(Krasnopolsky, 2009) (molecules cm <sup>-2</sup> s <sup>-1</sup> )	(Cordier et al., 2009) (molecules cm <sup>-2</sup> s <sup>-1</sup> )	(Willacy et al., 2016) (molecules cm <sup>-2</sup> s <sup>-1</sup> )	State at Titan STP (1.5 bar, 94 K)
C <sub>2</sub> H <sub>6</sub> (ethane)	1.17 x 10 <sup>9</sup>	3.40 x 10 <sup>9</sup>	N/A	Liquid
C <sub>2</sub> H <sub>2</sub> (acetylene)	3.22 x 10 <sup>8</sup>	5.10 x 10 <sup>7</sup>	N/A	Solid
C <sub>3</sub> H <sub>8</sub> (propane)	2.17 x 10 <sup>8</sup>	3.30 x 10 <sup>8</sup>	N/A	Liquid
HCN (hydrogen cyanide)	1.54 x 10 <sup>8</sup>	1.30 x 10 <sup>8</sup>	1.20 x 10 <sup>8</sup>	Solid
HNC (hydrogen isocyanide)	N/A	N/A	8.10 x 10 <sup>6</sup>	Solid
C <sub>4</sub> H <sub>6</sub> (butadiene)	1.71 x 10 <sup>7</sup>	N/A	N/A	Solid
C <sub>2</sub> H <sub>3</sub> CN (acrylonitrile)	1.62 x 10 <sup>7</sup>	N/A	1.50 x 10 <sup>7</sup>	Solid
CH <sub>3</sub> CN (acetonitrile)	1.27 x 10 <sup>7</sup>	4.40 x 10 <sup>6</sup>	2.80 x 10 <sup>5</sup>	Solid
CH <sub>3</sub> C <sub>2</sub> CN (methylcyanoacetylene)	N/A	N/A	4.50 x 10 <sup>6</sup>	Solid(?)
HC <sub>3</sub> N	1.26 x 10 <sup>7</sup>	N/A	2.90 x 10 <sup>7</sup>	Solid

(cyanoacetylene)				
HC <sub>5</sub> N (2,4-pentadiynenitrile)	N/A	N/A	2.40 x 10 <sup>6</sup>	Solid(?)
C <sub>2</sub> N <sub>2</sub> (cyanogen)	3.52 x 10 <sup>6</sup>	N/A	5.80 x 10 <sup>5</sup>	Solid
C <sub>3</sub> H <sub>4</sub> (propadiene)	2.64 x 10 <sup>6</sup>	N/A	N/A	Solid
CO <sub>2</sub> (carbon dioxide)	2.04 x 10 <sup>6</sup>	1.30 x 10 <sup>6</sup>	N/A	Solid
C <sub>6</sub> H <sub>6</sub> (benzene)	1.08 x 10 <sup>6</sup>	1.00 x 10 <sup>6</sup>	N/A	Solid
C <sub>4</sub> H <sub>8</sub> (butene)	9.24 x 10 <sup>5</sup>	6.20 x 10 <sup>7</sup>	N/A	Solid (2-butene), liquid ((1-butene))
C <sub>2</sub> H <sub>5</sub> CN (propionitrile)	8.00 x 10 <sup>5</sup>	N/A	6.4 x 10 <sup>6</sup>	Solid
C <sub>4</sub> H <sub>10</sub> (butane)	7.02 x 10 <sup>5</sup>	5.40 x 10 <sup>7</sup>	N/A	Solid
C <sub>4</sub> H <sub>2</sub> (diacetylene)	4.09 x 10 <sup>5</sup>	N/A	N/A	Solid
C <sub>4</sub> H <sub>4</sub> (butatriene)	1.57 x 10 <sup>4</sup>	N/A	N/A	Solid (?)

411

412 Table 2 – A list of structures of possible solids on the surface of Titan, as determined  
 413 from the Cambridge Structural Database (CSD) version 5.37 (Groom et al., 2016). \*  
 414 indicates structure determined at non-ambient pressure and \*\* indicates an entry not  
 415 in CSD version 5.37 as only recently deposited. Additionally, we are aware that a  
 416 structure of propionitrile has recently been determined (Ennis, 2017). \*\*\*The focus  
 417 of this contribution has been a survey of the potential organic solid component of  
 418 Titan, hence the use of the CSD as a search tool. However, it should be noted that  
 419 hydrates only fit into the remit of the CSD collection if they contain an organic  
 420 component - hence the limited number listed here (for instance there are no ammonia  
 421 hydrates in the CSD). The reader is directed to the Inorganic Crystal Structure  
 422 Database (Rühl) for further information on hydrate materials, and to the American  
 423 Mineral Database for information on Earth's organic-molecule containing minerals  
 424 (Downs and Hall-Wallace, 2003).

Material	CSD Refcode	Temperature structure determined at (K)	Density (gcm <sup>-3</sup> )	Notes
<b>Molecular Solids</b>				
C <sub>2</sub> H <sub>6</sub> (ethane)	ETHANE	90	0.669	
C <sub>2</sub> H <sub>6</sub> (ethane)	ETHANE01	85	0.719	
C <sub>2</sub> H <sub>6</sub> (ethane)	ETHANE02	295	0.708	
C <sub>2</sub> H <sub>6</sub> (ethane)	ETHANE03	90	0.668	
C <sub>2</sub> H <sub>2</sub> (acetylene)	ACETYL	156	0.747	
C <sub>2</sub> H <sub>2</sub> (acetylene)	ACETYL01	141	0.765	
C <sub>2</sub> H <sub>2</sub> (acetylene)	ACETYL02	131	0.764	
C <sub>2</sub> H <sub>2</sub> (acetylene)	ACETYL03	141	0.76	
C <sub>3</sub> H <sub>8</sub> (propane)	JAYDUI	30	0.803	
HCN (hydrogen cyanide)				No CSD structure
HNC (hydrogen isocyanide)				No CSD structure

C <sub>4</sub> H <sub>6</sub> (butadiene)	ZZZUPG	295	0.975	
C <sub>2</sub> H <sub>3</sub> CN (acrylonitrile)	POQMIR	153	1.027	
CH <sub>3</sub> CN (acetonitrile)	QQQCIV	77	1.198	
CH <sub>3</sub> CN (acetonitrile)	QQQCIV01	215	1.022	
CH <sub>3</sub> CN (acetonitrile)	QQQCIV03	208	1.025	
CH <sub>3</sub> CN (acetonitrile)	QQQCIV04	206	1.058	
CH <sub>3</sub> CN (acetonitrile)	QQQCIV05	201	1.028	
CH <sub>3</sub> CN (acetonitrile)	QQQCIV06	296	1.091	
CH <sub>3</sub> CN (acetonitrile)	QQQCIV07	296	1.104	
CH <sub>3</sub> CN (acetonitrile)	QQQCIV08	296	1.216	
CH <sub>3</sub> C <sub>2</sub> CN (methylcyanoacetylene)				No CSD structure
HC <sub>3</sub> N (cyanoacetylene)	CAACTY	295	1.075	
HC <sub>5</sub> N (2,4-pentadienenitrile)				No CSD structure
C <sub>2</sub> N <sub>2</sub> (cyanogen)	CYNGEN	295	1.25	
C <sub>3</sub> H <sub>4</sub> (propadiene)				No CSD structure
CO <sub>2</sub> (carbon dioxide)	SACBAA	680	2.826	*
CO <sub>2</sub> (carbon dioxide)	SACBAA01	680	2.831	*
C <sub>6</sub> H <sub>6</sub> (benzene)	BENZEN	218	1.055	
C <sub>6</sub> H <sub>6</sub> (benzene)	BENZEN01	138	1.094	
C <sub>6</sub> H <sub>6</sub> (benzene)	BENZEN02	270	1.024	
C <sub>6</sub> H <sub>6</sub> (benzene)	BENZEN03	295	1.259	
C <sub>6</sub> H <sub>6</sub> (benzene)	BENZEN04	295	1.259	
C <sub>6</sub> H <sub>6</sub> (benzene)	BENZEN05	295	1.173	
C <sub>6</sub> H <sub>6</sub> (benzene)	BENZEN08	295	1.561	
C <sub>6</sub> H <sub>6</sub> (benzene)	BENZEN09	295	1.812	
C <sub>6</sub> H <sub>6</sub> (benzene)	BENZEN10	295	1.263	
C <sub>6</sub> H <sub>6</sub> (benzene)	BENZEN11	296	1.157	*
C <sub>6</sub> H <sub>6</sub> (benzene)	BENZEN12	296	1.205	*
C <sub>6</sub> H <sub>6</sub> (benzene)	BENZEN13	296	1.139	*
C <sub>6</sub> H <sub>6</sub> (benzene)	BENZEN15	295	1.07	*
C <sub>6</sub> H <sub>6</sub> (benzene)	BENZEN16	295	1.195	*
C <sub>6</sub> H <sub>6</sub> (benzene)	BENZEN17	295	1.202	*
C <sub>6</sub> H <sub>6</sub> (benzene)	BENZEN18	150	1.05	*
C <sub>4</sub> H <sub>8</sub> (1-butene)				No CSD structure
C <sub>4</sub> H <sub>8</sub> (2-butene)				No CSD structure
C <sub>2</sub> H <sub>5</sub> CN (propionitrile)				No CSD structure
C <sub>4</sub> H <sub>10</sub> (butane)	DUCKOB04	90	0.807	
C <sub>4</sub> H <sub>2</sub> (diacetylene)				No CSD structure
C <sub>4</sub> H <sub>4</sub> (butatriene)				No CSD structure
<b>Molecular co-crystals</b>				



1:1 acetylene methanol	CIYYEP	155	0.878	
1:1 benzene : acetylene	ELIQIZ	123	1.01	
1:1 benzene : acetylene	ELIQIZ01	201	0.987	
1:1 acetylene : ammonia	FOZHOS	143	0.834	
1:1 acetylene : ammonia	FOZHOS01	143	0.834	
2:1 acetylene : acetonitrile	GURMUC	159	0.862	
1:1 acetylene : phenol	GURNAJ	143	1.19	
1:1 acetylene : formaldehyde	GURNEN	123	0.925	
1:1 acetylene : 1,3- xylene	GURNIR	168	0.982	
1:2 acetylene mesitylene	GURNOX	153	0.982	
1:2 acetylene : acetone (alpha)	TACRUL	159	0.934	
1:1 acetylene : acetone (beta)	TACSAS	159	0.93	
2:1 acetylene : pyridine	WAFNIB	185	1.005	
1:2 acetylene : 2,5- dimethylpyrazine	WAFNOH	153	1.104	
1:2 acetylene : 2,5- dimethylpyridine	WAFNUN	205	1.025	
1:3 acetylene : hydroquinone	ZZZVKY	295	1.358	
3:1 benzene : ethane	UKACAM	90	1.067	**
1:4 1,3-butadiene : urea	ZZZAJV	153	1.526	
1:1 acetonitrile : 3,4- Dihydroxybenzoic acid	EDUWUW	120	1.426	
1:1:1 acetonitrile : Cyclohexane- 1,3cis,5cis- tricarboxylic acid	GUTRUI	180	1.367	
1:2:1 acetonitrile : 4- Hydroxybenzoic acid 2,3,5,6- tetramethylpyrazine	HONTIO	100	1.275	
1:3 acetonitrile : hydroquinone	HQUACN	295	1.341	
1:3 acetonitrile : hydroquinone	HQUACN01	295	1.336	

1:1 acetonitrile : 4H-1,2,4-Triazol-4-amine	IHAYAS	153	1.296	
1:0.5 Benzene-1,2,3-tricarboxylic : acetonitrile	YECBOY	160	1.536	
1:1 4-phenoxyphenol carbon dioxide	QIRKUZ	100	1.322	
1:1 4-phenoxyphenol : carbon dioxide	QIRLAG	100	1.349	
1:1 4-phenoxyphenol : carbon dioxide	QIRLEK	100	1.355	
1:1 Hydroquinone : carbon dioxide	ZZZVLW	295	N/A	No atomic co-ordinates in CSD
1:1 N,N-Diethyl-beta-alanine : benzene	DEBALB	160	1.133	
1:1 1,2-diphenylacetylene : benzene	KURCEG	173	1.157	
2:1 trimethyl-acetic acid : benzene	TMACBZ	278	1.051	
6:1 5-methyl-1,3-cyclohexanedione : benzene	VEVJOV	188	1.237	
<b>Hydrates ***</b>				
Ethane clathrate hydrate	IKAVOF	293	0.984	
Ethane clathrate hydrate	QQQFNM	295	N/A	No atomic co-ordinates in CSD
Acetylene (2,5-dimethylpyridine) dihydrate	WAFPAV	205	1.085	
acetylene clathrate hydrate	NAHCIJ	143	1.003	
propane clathrate hydrate	NAHCOP	123	0.919	
Methane propane clathrate hydrate	NAHCUV	163	0.994	
carbon dioxide clathrate hydrate	LURDOT	N/A	1.144	

425

426

427

428 Figure 1 – Comparison of mineral processes on Earth with that of Titan. Though there is  
429 much that they have in common, such as ‘hydrological’ cycling, the temperatures and  
430 dominant chemistry of the surface and sub surfaces of these planetary bodies are very  
431 different.

432

433 Figure 2 – Presentations of the crystal structure of three molecular solids that could be present  
434 on Titan, a) the crystal structure of acetylene (CSD refcode ACETYL), b) the crystal structure  
435 of propane (refcode JAYDUI) and c) acetonitrile (refcode QQQCIV01). In each of the  
436 images grey spheres represent carbon atoms, white hydrogen atoms, and blue represent  
437 nitrogen atoms.

438

439

440 Figure 3 – Two molecular co-crystals that have already been identified between species listed  
441 in Table 1, a) 2:1 acetylene : acetonitrile (CSD refcode GURMUC) and b) 3:1 benzene :  
442 ethane (refcode UKACAM). In each of the images grey spheres represent carbon atoms;  
443 white hydrogen and blue represent nitrogen atoms.

444

445

446 Figure 4 – Two possible Titan hydrate materials a) acetylene clathrate hydrate (CSD refcode  
447 NAHCIJ) and b) ammonia monohydrate II (Fortes et al., 2009). In each of the images grey  
448 spheres represent carbon atoms, white hydrogen, red oxygen and blue represent nitrogen  
449 atoms.







