



High Pressure Solid State
Structures of Simple Molecules

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Introduction

Many di- and triatomic compounds have simple molecular structures under ambient conditions . We think immediately of gases such as carbon dioxide , carbon monoxide , the oxides of sulfur and nitrogen , and other such typical covalent compounds .

On the other hand , there are probably just as many covalently bonded materials , also with simple empirical formulas , that are **nonmolecular solids** with extended , or “infinite” atomic lattices . The diamond and graphite structures , both covalently bonded , are good examples . Solids with predominately ionic bonding , such as common salt , sodium chloride , are also nonmolecular solids . There are simple compounds like zinc oxide and sulfide that have a “mixed” sort of bonding , partly ionic , partly covalent , with extended lattices . And of course , there are the metals and metalloids , having their own characteristic crystal structures .

I was musing why don't the simple molecular compounds have extended lattices , too ? Would it be possible to tremendously compress them into nonmolecular solids , and if so , what structure would they assume ? Can we rationally predict the correct structure for such a compound ?

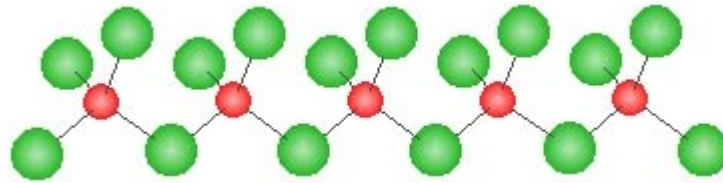
In this brief essay I'll examine several common molecular compounds and try to make an “educated guess” as to what they would look like under the very high-pressure conditions that might convert them into nonmolecular solids with extended atomic lattices .

Chromium trioxide

Chromium(VI) oxide , CrO_3 , is an inorganic “polymer” , in the sense that it consists of long Cr-O chains with covalent bonding . The compound is a dark reddish-purple solid , m.p. $195\text{ }^\circ\text{C}$, dec. $250\text{ }^\circ\text{C}$, soluble in water and in

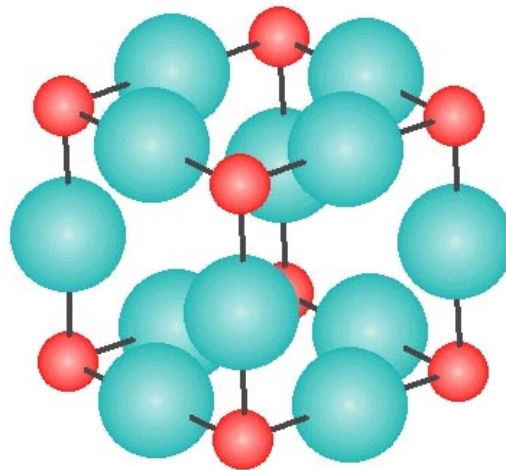
some organic solvents . It is a very powerful oxidizer , reacting vigorously with many organic compounds .

The chromium(VI) atoms [red] in the chains have a tetrahedral coordination by neighboring oxygen atoms [green] (ref. 1 , [page 13](#)) :



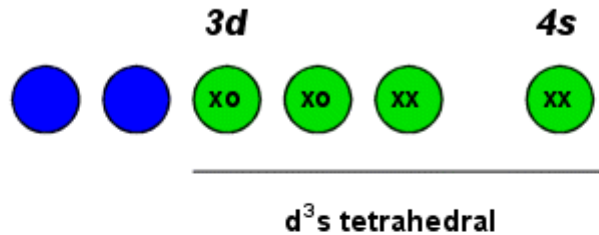
The chromiums probably are using a d^3 tetrahedral hybrid MO ; the lower oxygens in the sketch are likely also tetrahedral (sp^3) . A suggested electronic structure for the chromium in CrO_3 is shown in the sketch at the top of the following page .

The related heavier analogue compound ReO_3 is a nonmolecular solid with an extended atomic lattice having a cubic structure :



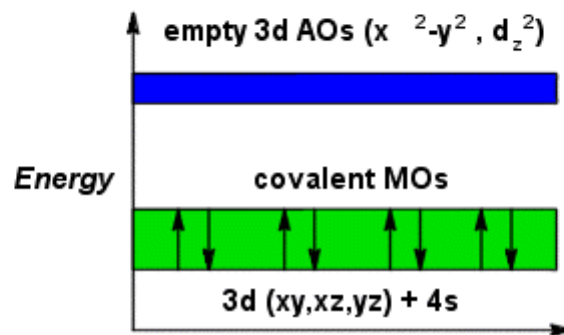
In the above M3D crystal model , the small red spheres represent the rhenium(VI) atoms , which are octahedrally coordinated by the large aqua spheres , representing the covalent linear (sp) oxygen linking atoms .

Proposed Electronic Structure of Chromium Atoms in Chromium Trioxide



x = chromium valence electrons

o = oxygen links' valence electrons

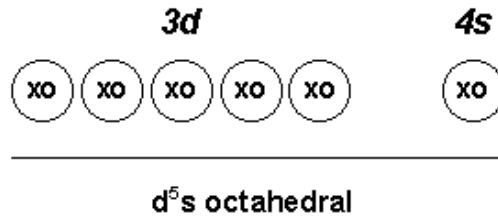


In the above electronic structure sketch, the “xo” orbital lobes would be for the chain Cr-O bonds; the “xx” orbital lobes would be for the axial Cr-O bonds in the CrO_3 sketch on the previous page. That is, the two axial Cr-O bonds would be **coordinate covalent**, $\text{Cr} \rightarrow \text{O}$. Also note in the energy drawing that in a tetrahedral environment, the $3d_{xy,xz,yz}$ AOs are of higher energy than the $3d_{x^2-y^2, z^2}$ AOs. They will be combined with the 4s AO to form the tetrahedral d^3s hybrid MO, which will now be at a **lower** energy level than the unused, empty x^2-y^2 and z^2 AOs.

The heavier Group 6B trioxides, MoO_3 and WO_3 , also have distorted ReO_3 crystal structures under ambient conditions. I was wondering if CrO_3 was very strongly compressed, would it too assume the ReO_3 crystal

structure ? In this case its electronic structure would be somewhat different , and simpler than in the covalent polymer's case :

Proposed Electronic Structure of Chromium Atoms in Chromium Trioxide (ReO_3)



x = chromium valence electrons

o = oxygen links' valence electrons

The more compact ReO_3 crystal structure should be favored at high pressure rather than the polymeric chain form of CrO_3 . The question then arises : why is the polymeric chain structure the stable form under ambient conditions ? Perhaps the Cr(VI) atom is too small to fit comfortably into the ReO_3 cubic structure , and doesn't bond as strongly with the neighboring oxygen atoms as in the polymeric chain . Here are several representative **crystal ionic radii** for small metal cations (per Shannon-Prewitt) :

Chromium(IV) , octahedral : 0.69 Å
 Chromium(VI) , octahedral : 0.58 Å
 Chromium(VI) , tetrahedral : 0.40 Å
 Molybdenum(VI) , octahedral : 0.73 Å
 Tungsten(VI) , octahedral : 0.74 Å
 Rhenium(VII) , octahedral : 0.67 Å
 Aluminum(III) , octahedral : 0.675 Å

These figures suggest that because the Cr-O bond in the chains is shorter (0.40 Å) than that in the ReO_3 cubic structure (0.58 Å) , it is stronger in them than in the latter form . That might make the chains more thermodynamically stable than the cubic structure . In any case , the ReO_3 form of CrO_3 would surely have significantly different physical and

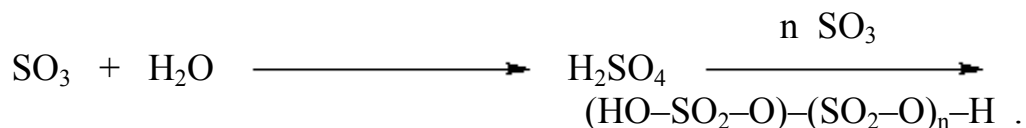
chemical properties than conventional CrO_3 . It should have a very low solubility in water and be a much less active oxidizing agent than the polymeric chain form .

Sulfur Trioxide

Sulfur trioxide is most familiar as a fuming , colorless liquid , m.p. $17\text{ }^\circ\text{C}$, b.p. $45\text{ }^\circ\text{C}$, but it can also exist as a stable solid in two forms , α and β , both of which have an “asbestos-like” appearance of fine , long , silky , white fibers , with melting points of $62\text{ }^\circ\text{C}$ and $32\text{ }^\circ\text{C}$, respectively . The crystal structure of the β modification is somewhat like that of CrO_3 (sketch on [page 3](#)) , except that a regular twisting in the S-O-S bonds results in a helical chain , like the threads of a screw [Wells , ref. 1 , [page 13](#) ; see his Figure 139(b) , p. 430] . Wells comments ,

“..... SO_3 exists in a number of polymorphic forms and the forms differ appreciably in their stability towards moisture” (p. 430) .

It is known that contamination of liquid SO_3 – the γ modification – by moisture can convert it into one of the fibrous forms . Perhaps the sulfuric acid intermediate is catalyzing the polymerization reaction :

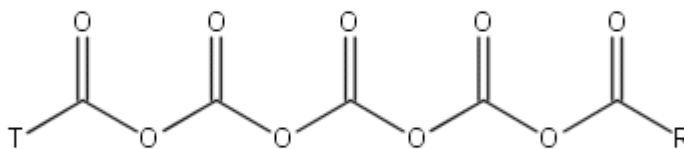
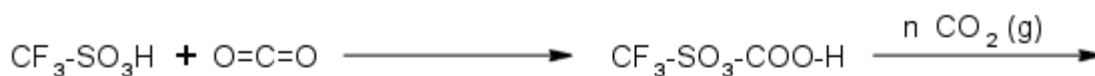


Once again , I wondered if a high pressure treatment would convert the liquid or even fibrous form into the nonmolecular ReO_3 crystal structure . As with CrO_3 , this would dramatically reduce the high reactivity of the normal SO_3 liquid and fibrous types . I am reminded of the comparison between the violently reactive SF_4 and remarkably inert SF_6 gases . The former reagent’s molecules are “see-saw” shaped , while the sulfur atom in SF_6 is octahedrally bonded by six fluorine atoms , which shield the electrophilic

sulfur from attacking nucleophiles . A similar shielding effect should be observed in the hypothetical ReO_3 form of SO_3 .

Carbon Dioxide

Carbon dioxide can exist in a solid form , “dry ice” , but it is a molecular solid (ref. 2 , [page 13](#)) . I wondered if , under great pressure , dry ice might be converted into a fibrous polymer like $\beta\text{-SO}_3$, for example :

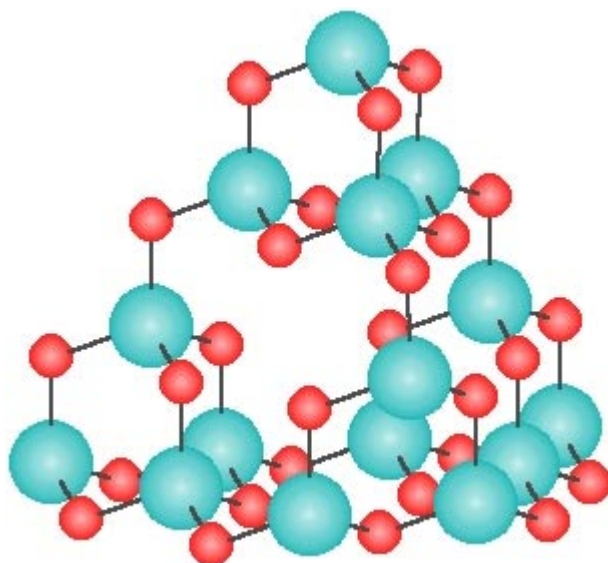


Poly(carbonic anhydride)

T = triflate R = extended polymer chain

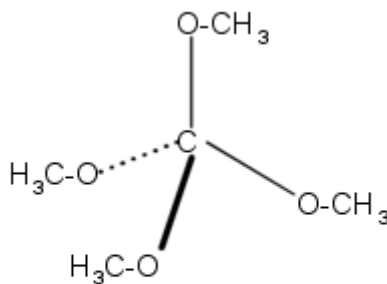
The SO_3 polymerization mechanism noted above , using sulfuric acid as an “initiator” to start the chain growth , might have a parallel in the hypothetical CO_2 polymerization . A very small quantity of a strong acid , such as trifluoromethanesulfonic acid , $\text{CF}_3\text{-SO}_3\text{H}$, could be tried as a catalyst to help polymerize the dry ice under pressure . The ends of the fiber chains would require capping by protons , as shown in the sketch , which might also improve the stability of the chains by preventing them from spontaneously unzipping to CO_2 molecules .

Extending this scenario , would it be possible to polymerize carbon dioxide to a solid isostructural with silica ? An M3D model of this crystal structure is shown on the next page . **N.B.** See reference 4 on [page 14](#) , below .



In this M3D model of silica , the larger cyan spheres represent silicon(IV) , which are tetrahedrally coordinated by covalent oxygen linking atoms (the smaller red spheres) . The oxygens are shown as being bent , that is , with a tetrahedral coordination ; in certain modifications of silica the oxygen links are linear , and in other forms there is a “blend” of Si-O-Si bond angles .

It is noteworthy in this context that the $C-(O)_4$ atomic cluster is well-known in organic chemistry , being present in the **orthocarbonate esters** , which are quite stable compounds :



Tetramethyl Orthocarbonate

M.W. 136.15 b.p. 114 C

Experimentally , a small pellet of dry ice , possibly with liquid nitrogen cooling , would be strongly compressed in a tetrahedral anvil press . Conditions used in the high-pressure conversion of graphite to diamond could be tried in the compression of the dry ice pellet .

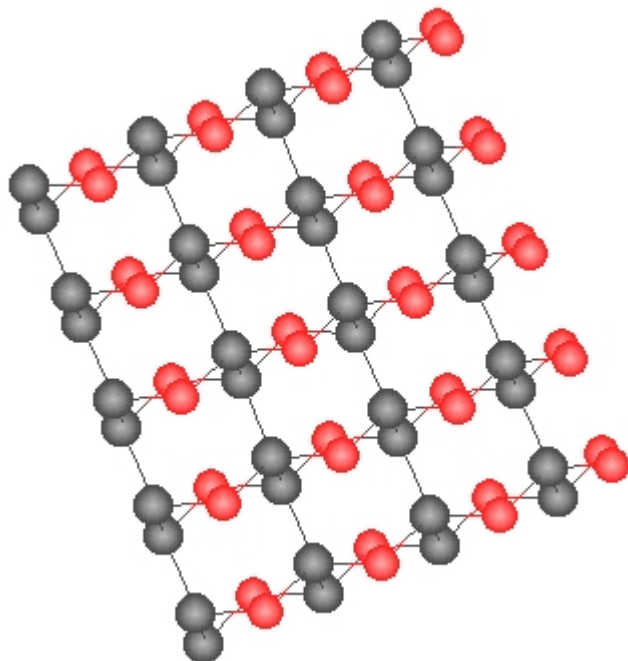
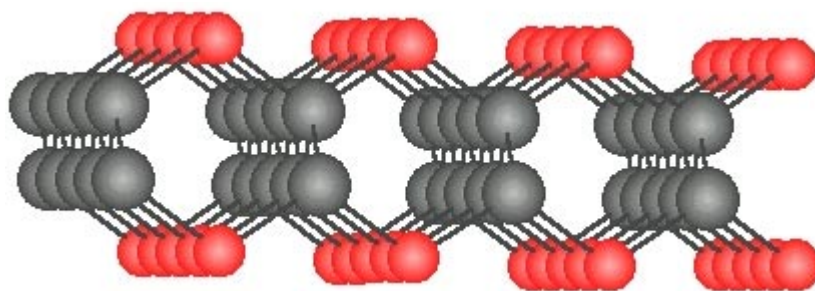
The graphite-to-diamond transformation is a good example of the formation of a **metastable** solid . Although diamond is thermodynamically less stable than graphite , the kinetics of its conversion to graphite are infinitely slow at STP , and so diamonds can exist indefinitely under normal conditions . We might discover that solid CO₂ with an extended atomic lattice is similarly metastable ; once it is created at extremely high pressures , it might resist Peierls distortion ([page 11](#)) indefinitely and so have a stable existence under ambient conditions .

Experimentally , liquid hydrogen has been converted into a solid , metallic allotrope , albeit in tiny quantities that had an ephemeral existence (ref. 3 , [page 13](#)) . This gives us some small encouragement that the synthesis of polymeric carbon dioxide may not be a mere daydream , after all .

Carbon monoxide

Again , this is purely hypothetical , but carbon monoxide could conceivably be polymerized under high pressure , possibly with a catalyst , to a nonmolecular solid . With purely covalent bonding , carbon requires four bonds , while oxygen requires two per atom . The way out of this predicament for CO is to have carbon bond half **with itself** and the other half with oxygen . With this requirement in mind , I built up an M3D molecular model of a possible carbon monoxide polymer (shown on the next page) . **N.B.** See [page 15](#) below for an alternative structure of poly(CO) .

As you can see , this would be a sheet-like substance , somewhat like graphite , with layers built from “sandwiches” of O–C–C–O :

[Top View of $(CO)_x$][Side View of $(CO)_x$]

In each sheet of the polymer, there would be parallel chains of carbon atoms (black spheres) having a tetrahedral coordination, which are bonded side-by-side by bridging oxygen linking atoms (red spheres), bonding two-fold to carbon. Since the oxygens could participate in external bonding with many solvents and reagents, including hydrogen bonding and coordination, the polymer sheets might find many uses in chemical research and technology. It certainly would be an interesting system to investigate.

What might prevent several, if not all, of the nonmolecular systems discussed above from forming, is the phenomenon of **Peierls distortion**, which was first proposed by the British solid state physicist Sir Rudolph E. Peierls in 1955 with regard to one-dimensional metallic solids. According to the “Peierls theorem”, such materials should be inherently unstable, and the metallic bond in them would either disappear, or never would form in the first place. Since then, and in recent decades, Peierls distortion has been recognized in two- and three-dimensional solid state systems as a general phenomenon that may effect the chemical bonds in many different types of materials, not only in metals.

I mentioned metallic hydrogen above. Let’s imagine a small sample of it sitting on my desk here; of course, its existence would be highly transitory, to say the least. Poof! Peierls distortion would cause the metallic bond in the sample to almost instantaneously disappear, to be replaced by localized sigma MOs between pairs of hydrogen atoms. The resulting hydrogen molecules would then fly away in every direction at a great speed.

A similar sort of thing might readily occur in the nonmolecular systems we looked at above. For example, the silica form of solid CO_2 might be created at very high pressures, possibly with a suitable catalyst present. However, like metallic hydrogen, as soon as the pressure on the sample is released, Peierls distortion would cause the carbon dioxide molecules rapidly, if not almost instantaneously, to reform and disperse.

The underlying foundation of Peierls distortion is first, the relative thermodynamic stabilities of the molecular, as opposed to the nonmolecular modifications of the compound; and second, the energetics and kinetics of the conversion of the nonmolecular to the molecular form. For example, graphite is known to be thermodynamically more stable than the diamond allotrope of carbon. However, the energetics and kinetics of the conversion of diamond to graphite are too formidable for this transformation to spontaneously occur under ambient conditions. We are thus quite familiar with diamonds, both as chemists, and maybe a few of the readers on a personal basis as well. Diamond is said to be a **metastable** material.

It may well be, then, that at least several of the systems discussed in this report may be metastable materials, like diamond. For example, I think that poly(carbon monoxide), $(\text{CO})_x$, may be one such material. The C–C and C–O bonds in it are quite strong, and they are unstrained. If this polymer can indeed be synthesized, I think it would be quite stable under ambient conditions. Mind you, it might decompose to CO at elevated temperatures, but as I suggested, its room temperature chemistry could be both varied and productive.

Similarly, I think that the ReO_3 forms of CrO_3 and SO_3 would be metastable thermodynamically, and physically and chemically stable in ambient conditions. The carbon dioxide linear chain polymer and silica forms would be the most dubious nonmolecular candidates proposed in this study, and in that sense their synthesis would present the greatest challenge to high pressure chemists.

What about other small molecules such as SO_2 , NO, and NO_2 ? Could supercompression convert them into metastable nonmolecular forms? In order for this to occur, I believe it would be necessary for them to be able to assume one of the well known, highly stable crystal structures familiar to solid state chemists. Unfortunately, a cursory analysis of these molecules suggests that they have **too many** valence electrons to be compatible with such crystal structures. The molecules “dispose” of excess valence electrons in lone pairs, an option rarely available in three-dimensional frameworks. That leaves us with the lower dimensional modifications, such as linear polymers exemplified by $-\text{[(S=O)–O]}_x$, $-\text{[(N=O)–O]}_x$, and the like. While not completely ruled out, these linear polymer chain forms are likely to be quite unstable, and might not be accessible under ambient conditions.

I nevertheless hope that this exposition on the potential of high pressure chemistry for synthesizing exotic new materials from simple, common molecules will stimulate the imagination and creativity of chemists in this field of study, and will encourage research and development in it.

(Several references follow on the next page).

References

1. A.F. Wells , Structural Inorganic Chemistry , 3rd ed. , Clarendon Press , Oxford , UK , 1962 ; CrO₃ is described on p. 442 ; SO₃ is described on pp. 430-431 .
2. G.E. Rodgers , Introduction to Coordination , Solid State , and Descriptive Inorganic Chemistry , McGraw-Hill , New York , 1994 ; the crystal structure of dry ice is sketched in Figure 7.24(a) , p. 179 .
3. S.T. Weir , A.C. Mitchell , and W.J. Nellis , “Metallization of Fluid Molecular Hydrogen at 140 GPa (1.4 Mbar)” , Phys. Rev. Lett. 76 (11) , pp. 1860-1863 (1996) ; see also , P.M. Celliers et al. , “Shock-Induced Transformation of Liquid Deuterium into a Metallic Fluid” , Phys. Rev. Lett. 84 (24) , pp. 5564-5567 (2000) .
 The team leader , William J. Nellis , has written a very clear , concise report on their research with metallic hydrogen , online at <http://www.llnl.gov/str/Nellis.html> ; his report is titled , “Jumpin’ Jupiter ! Metallic Hydrogen” . The Jupiter reference recalls the planetary science theory that the core of the planet Jupiter (and probably those of the other outer “gas giant” planets , Saturn , Uranus , and Neptune) is thought to be composed of very hot , supercompressed metallic hydrogen . The powerful magnetic fields around Jupiter might arise from this metallic core . In any case , I congratulate Dr. Nellis for his excellent presentation , clearly explaining the phenomenon of metallic hydrogen , and his research with it . His article is at the academic level of those published in , say , Scientific American and American Scientist magazines , and is fairly comprehensible to even a physics-deficient person like me . I wish other scientists would present their research work to the public , and to the world , in such a well-written and accessible style !

4. I have since learned that a nonmolecular, solid (but glassy) form of carbon dioxide has been produced by a team of Italian scientists in 2006. They named it “**amorphous carbonia**” : M. Santoro et al., “Amorphous Silica-like Carbon Dioxide”, Nature **441** (7095), pp. 857-860 (2006). See also the following Web articles :
 “Amorphous carbonia”, Wikipedia, the online encyclopedia, at http://en.wikipedia.org/wiki/Amorphous_carbonia ;
 “Carbon Dioxide Glass Created in the Lab”, New Scientist Tech, at <http://www.newscientisttech.com/article.ns?id=dn9339> ;
 “Dry Ice Creates Toughened Glass”, BBC news, at <http://news.bbc.co.uk/1/hi/sci/tech/5083222.stm> ; and ,
 “Dry Ice Forms Ultrahard Glass”, PhysicsWeb, at <http://physicsweb.org/articles/news/10/6/7/1> .
 This solid-state form of carbon dioxide was made by compressing dry ice at 40-50 GPa (up to about 500,000 atmospheres). However, it was unstable under ambient pressure, and reverted to molecular CO₂ (gas) when decompressed.

Interestingly, nitrogen can be supercompressed (110 GPa, about a million atmospheres) in a diamond anvil press and heated with a laser to 2000 K ; when cooled rapidly it forms **polymeric nitrogen**. This material is predicted to be stable at room temperature, and indeed is a remarkably hard solid, comparable to diamond : M.I. Eremets et al., “Single-bonded Cubic Form of Nitrogen”, Nature Materials **3**, pp. 558-563 (2004). See the Web article (a press release by the researchers announcing the discovery) at : <http://www.mpch-mainz.mpg.de/mpg/english/pri0804.htm>

See also the related Web article, “Nitrogen Power : New Crystal Packs a Lot of Punch”, by Alexandra Goho, Science News Online, at : <http://www.sciencenews.org/articles/20040717/fob4.asp> .

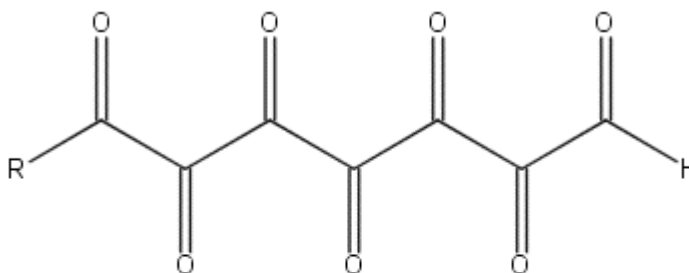
Each nitrogen atom in its crystal structure has three single bonds (sigma covalent) to other nitrogens. The nitrogens have a pyramidal structure, suggesting they are tetrahedrally (sp³) hybridized, with a lone pair of electrons at the apex of the pyramids.

An Internet search also revealed a theoretical study of poly(carbon monoxide) , $(\text{CO})_x$ (pages 9-10 above) :

G. Frapper et al. , “Can Carbon Monoxide Polymerize ? A Theoretical Investigation of Polyketone” , Chem. Commun. 1997 , pp. 2011-2012 . This article can be downloaded without charge from the Web at :

http://www.rsc.org/delivery/_ArticleLinking/DisplayArticleForFree.cfm?doi=a705721k&JournalCode=CC

As with the SO_3 (page 6) and linear CO_2 (page 7) polymers , formation and stabilization of linear CO polymer , as proposed by Frapper and co-authors , might be assisted by the inclusion of a small quantity of a strong acid , such as triflic acid ($\text{CF}_3\text{-SO}_3\text{H}$) , with the compressed carbon monoxide :



Polycarbonyl , $(\text{CO})_n$

(ends are capped with triflic acid ; $\text{R} = \text{CF}_3\text{-SO}_3^-$)

This latter linear structure might be a viable alternative to the graphite-sheet structure I described above on page 10 . In any case , it is encouraging to see that poly(CO) , in one form or another , may indeed be a reasonably stable material under ambient conditions .

Clearly , extraordinary transformations of simple molecules into remarkable new nonmolecular solids , both crystalline and glassy , can be accomplished by high-pressure chemistry techniques .