Methods in Chemistry III – Part 1
Modul M.Che.1101 WS 2010/11 – 10
Modern Methods of Inorganic Chemistry

Mi 10:15-12:00, Hörsaal II

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Crystal structure refinement

The atom coordinates x, y, z and displacement parameters U (isotropic) or U_{11}, U_{22}, … U_{23} (anisotropic, 6 parameters) are refined to minimize the sum of squared differences $\sum_{\text{reflections}} w\,(F_o^2 - F_c^2)^2$. For isotropic atoms:

$$A = \sum f_j \cos[2\pi(hx+ky+\ell z)]\, \exp(-8\pi^2 U \sin^2\theta/\lambda^2)$$

$$B = \sum f_j \sin[2\pi(hx+ky+\ell z)]\, \exp(-8\pi^2 U \sin^2\theta/\lambda^2)$$

$$F_c^2 = A^2 + B^2; \qquad \phi_c = \tan^{-1}(B/A)$$

Usually $R = \sum |F_o - F_c| / \sum |F_o|$ **serves as a quality control.**

However this *R-value* does not reflect the fact that the structure becomes more accurate when the data-to-parameter ratio increases. A better criterion for the precision of a crystal structure determination would be the standard deviation of a typical bond length!

Anisotropic motion

For anisotropic atoms, the isotropic term $\exp(-8\pi^2 U \sin^2\theta/\lambda^2)$ in the structure factor summation is replaced by:

$$\exp\{-2\pi^2[U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}\ell^2c^{*2}+2U_{23}k\ell b^*c^*+2U_{13}h\ell a^*c^*+2U_{12}hka^*b^*]\}$$

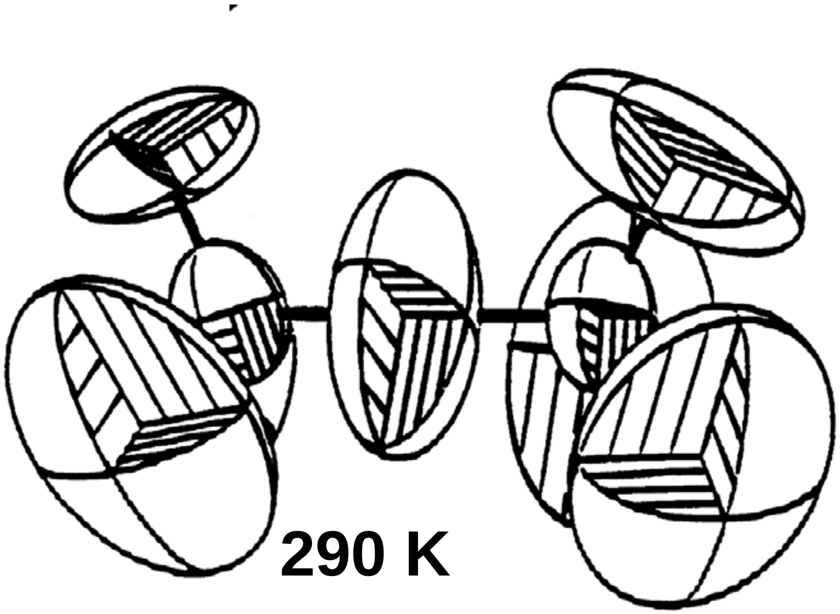
After an anisotropic refinement the atoms can be displayed as 50% *probability ellipsoids*; this is known as an ORTEP diagram. Large ellipsoids do not necessarily mean large motions; they can also be caused by unresolved disorder (two or more alternative atomic postions close to one another) or by a wrong element assignment (the atom should have fewer electrons, e.g. should be O rather than Cl).

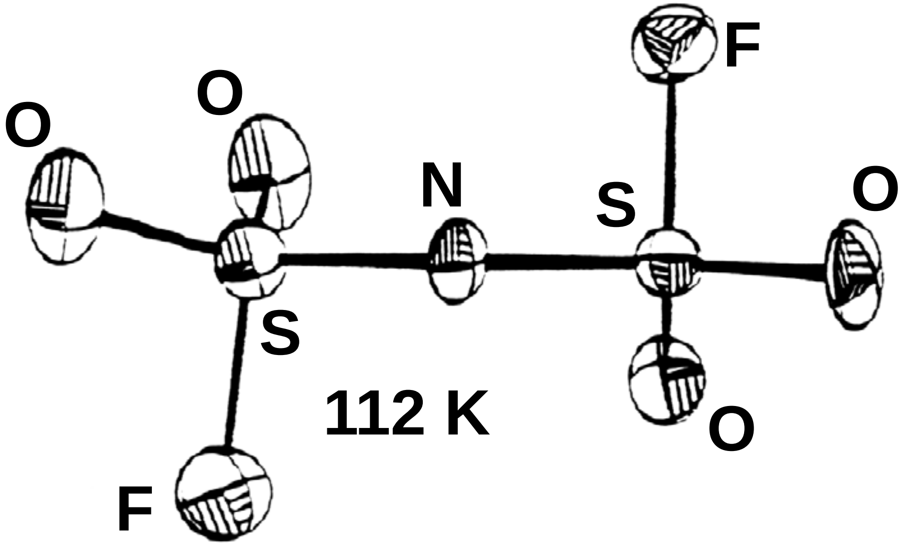
For 50% probability ellipsoids the chance is also 50% that the atom is somewhere else! For large ellipsoids one should also be careful not to over-interpret the third decimal place (in Å) of bond lengths.

Thermal ellipsoids and ORTEP diagrams

The very large ellipsoids observed for the anion $N(SO_2F)_2^-$ at 290 K may be the result either of large amplitude thermal motion or of an attempt to fit a single conformation to a disorder involving two or more components.

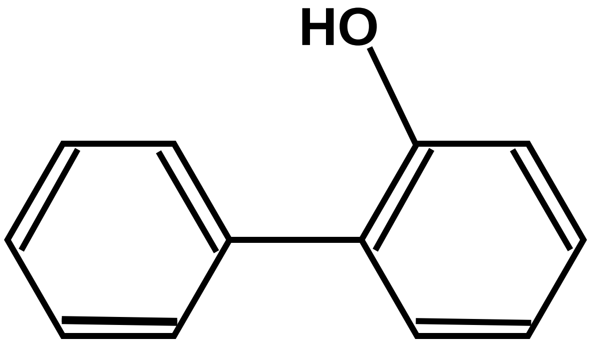
In this case the normal staggered structure at 112 K and the apparently eclipsed conformation at 290 K, as well as the observed bond lengths (S-O,F all in the range 1.24–1.36 Å at 290 K compared to S-F 1.57, S=O 1.42 Å at 112 K), indicate strongly that the 290 K structure is disordered.



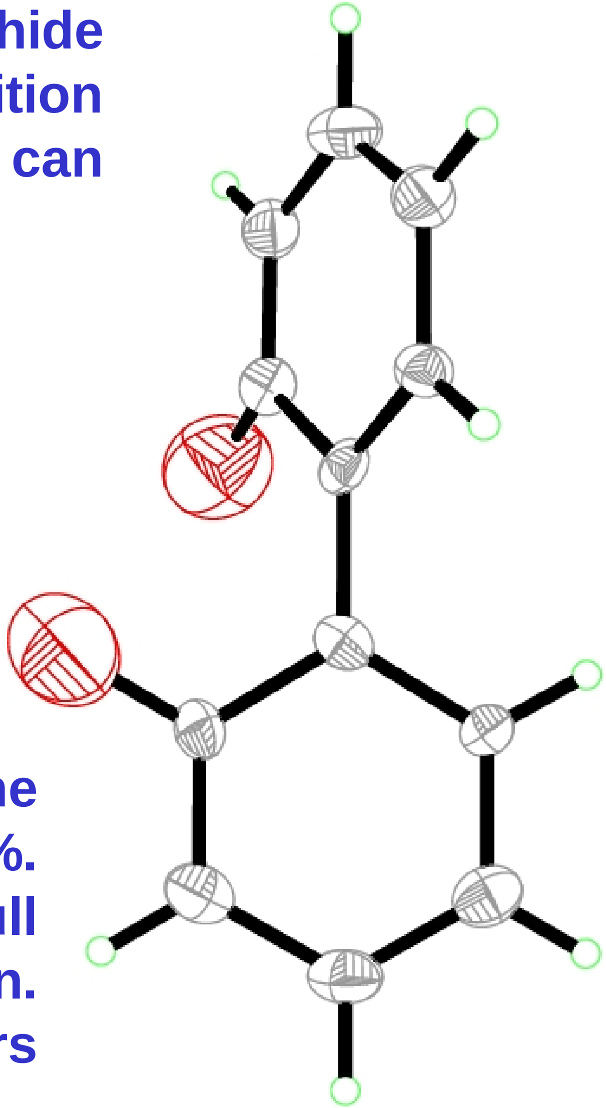


Displacement parameters and disorder

Unusual displacement parameters may well hide disorder. Often a molecule lies on a special position of higher symmetry than the molecule itself can possess. In this example the molecule:

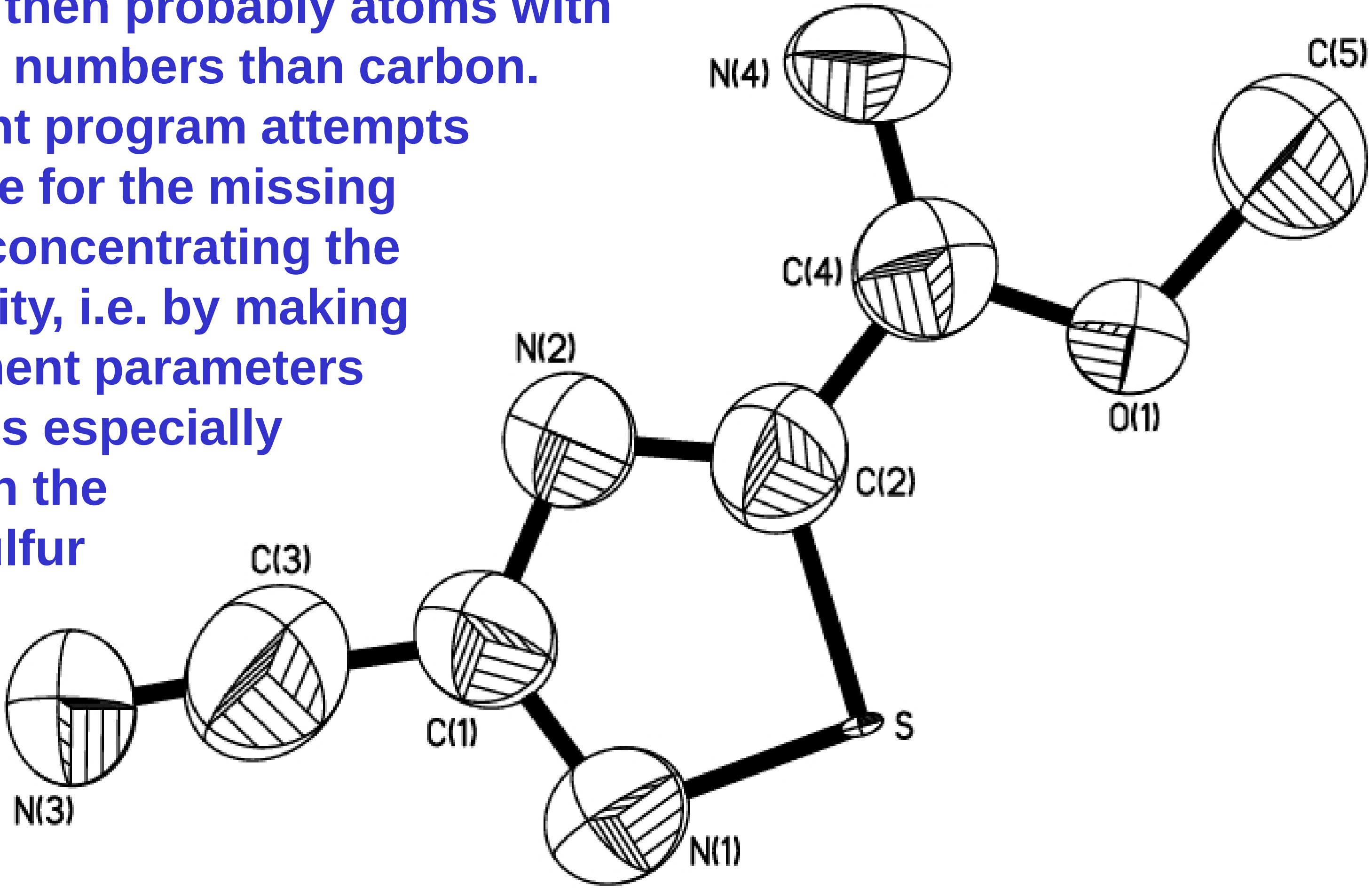


lies on a twofold axis, with the result that the oxygen atoms have effective occupancies of 50%. An attempt to refine the structure with full occupancies led to the **ORTEP** plot shown. Solvent toluene molecules on inversion centers are often disordered in a similar way.



The ORTEP plot as a diagnostic tool

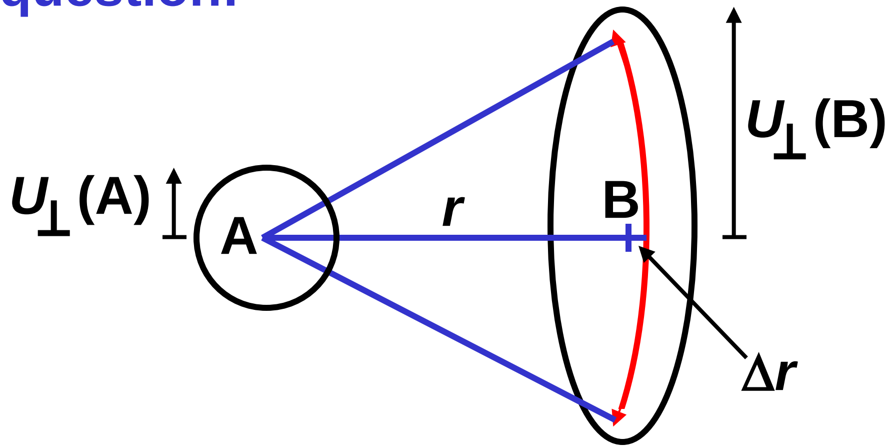
If the assignment of the atoms is not clear, one can try refining all atoms as carbon and then making an ORTEP plot with 50% probability ellipsoids. Atoms that are displayed as *smaller* ellipsoids are then probably atoms with *higher* atomic numbers than carbon. The refinement program attempts to compensate for the missing electrons by concentrating the electron density, i.e. by making the displacement parameters smaller. This is especially pronounced in the case of the sulfur atom in this example.



Libration

The higher the temperature, the smaller the bond lengths appear to be, even though the unit-cell usually gets larger! This is caused by molecular motion and especially by terminal atoms moving along the arc of a circle. These arcs are fitted by thermal ellipsoids, the centers of which must lie inside the circles in question:

$$\Delta r \simeq \frac{\Delta U}{2r} = \frac{[U_{\perp}(B) - U_{\perp}(A)]}{2r}$$

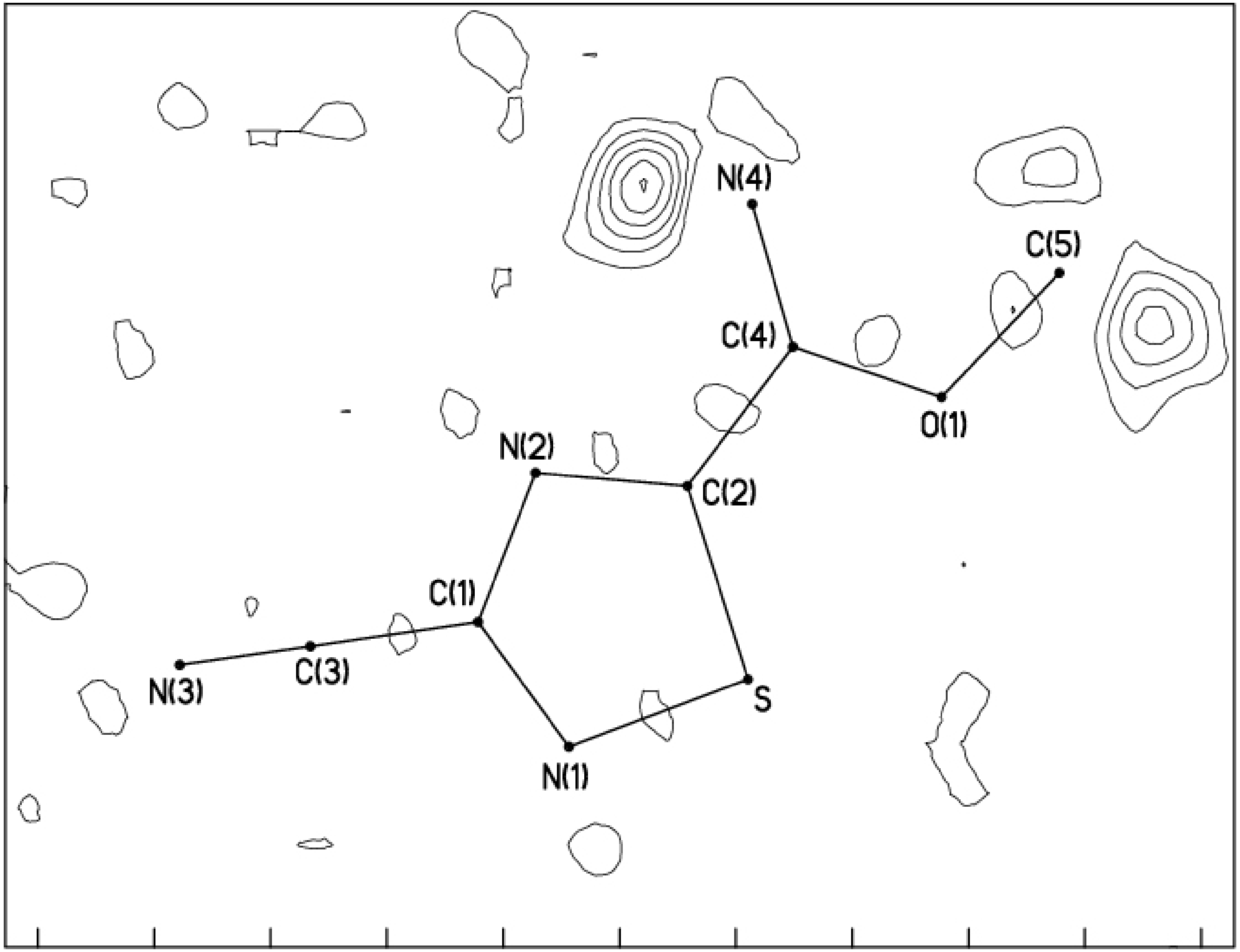


These corrections lie in the range 0.001 – 0.1 Å, depending on Δ*U*, which increases with increasing temperature. This effect is particularly large for small ions such as NO_3^-, BF_4^-, ClO_4^- and PF_6^-, and for $-CF_3$ groups.

In practice this *librational correction* is often ‘forgotten’. Of course it is always better to collect data at low temperature in order to reduce the correction and its associated uncertainty.

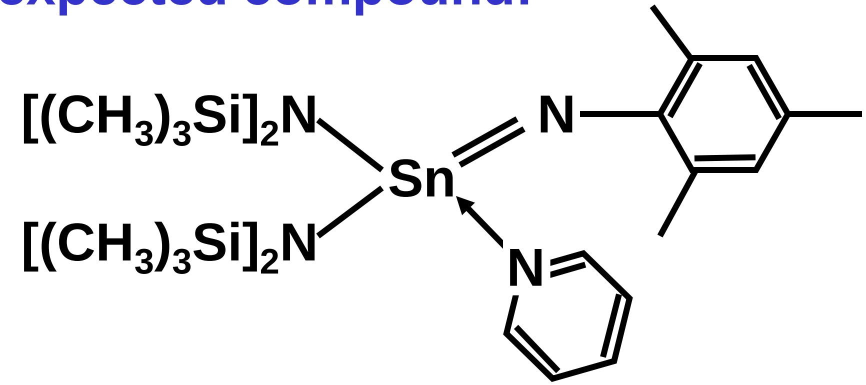
The difference electron density map

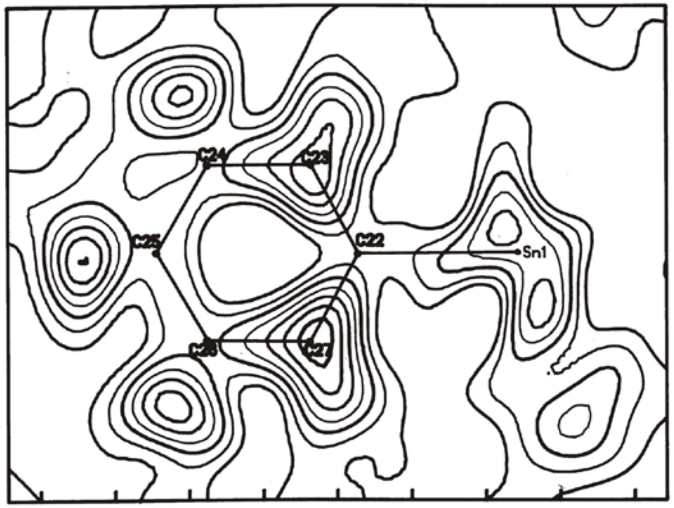
A Fourier synthesis with amplitudes $F_o - F_c$ and phases ϕ_c may be employed to find missing atoms (e.g. hydrogens). In this example two missing hydrogens lie in the plane shown: an imine hydrogen attached to N(4) and one of the three hydrogens of the methyl group C(5).



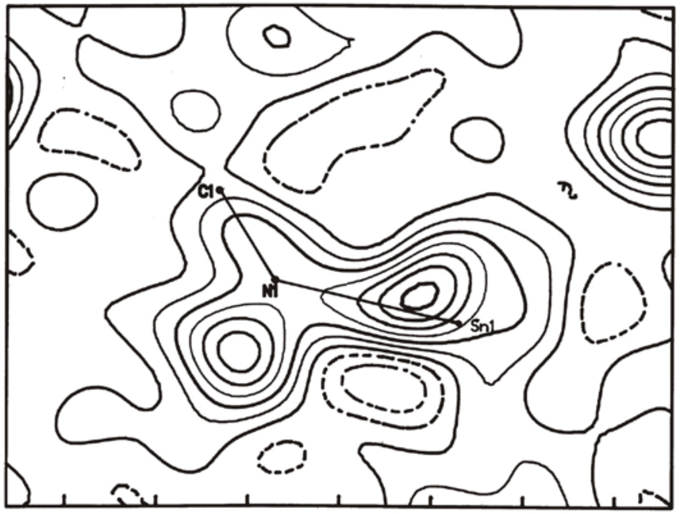
Example of a problematic atom assignment

For the expected compound:

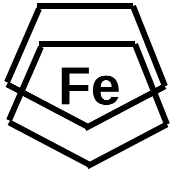




the structure was at first sight as expected. On closer examination, the N=Sn ‘double bond’ had the same length as the N—Sn single bonds. The difference electron density after a refinement with all atoms as carbon led to the solution of the riddle. The ring is bonded to Sn through a C atom and is disordered over two positions, rotated by 180° relative to each other. There is also a hydrogen atom attached to the N atom that now only makes a single bond to Sn.

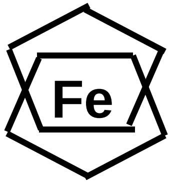


Ferrocene: eclipsed (D_{5h}) or staggered (D_{5d})?



D_{5h}

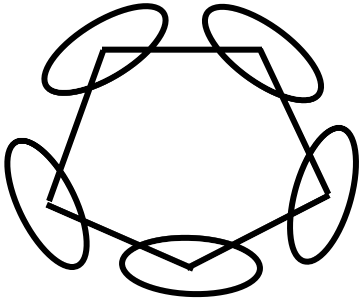
or



D_{5d}

The first structure determination (1956, room temperature) gave $Z = 2$ in $P2_1/c$. The molecule must then lie on an inversion center, so the structure '*must*' be staggered (D_{5d}). However electron diffraction in the gas phase (1968) showed approximately D_{5h} geometry.

The X-ray data at 293 K and 173 K (1979) were interpreted in terms of disorder (possibly of a D_{5h} structure), because the thermal displacement parameters of the carbon atoms remained very large even at low temperature.

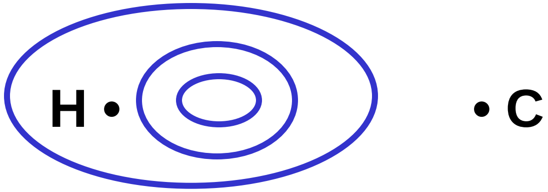


Two new low temperature phases were subsequently investigated. A triclinic phase at 164 K was almost D_{5h} (deviations $\Delta\phi$ ca. 9°), and an orthorhombic phase at 98 K was D_{5h} within experimental error.

Hydrogen atoms

The X-ray determination of hydrogen positions is inaccurate, because:

1. The scattering power of H-atoms is small.
2. The corresponding electron density is spread out and asymmetric. The center of gravity of this density is significantly shifted from the position of the hydrogen nucleus:

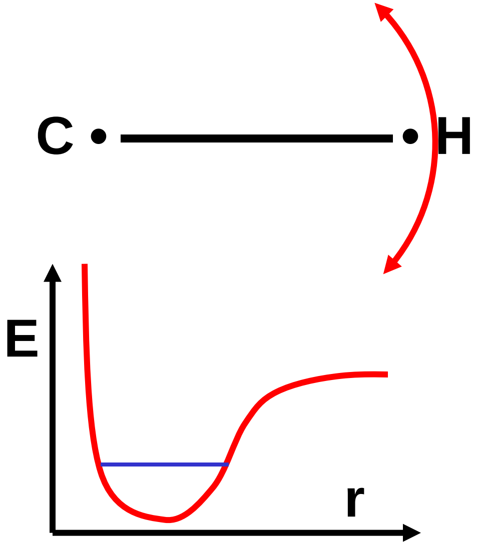


$\langle \mathrm{C—H} \rangle_{\text{X-ray}}$ ca. 0.96 Å

$\langle \mathrm{C—H} \rangle_{\text{neutron}}$ ca. 1.09 Å

Bonding electron density after subtracting the contribution of the carbon atom.

3. H-atoms are light and so have large vibrational amplitudes and correspondingly large librational corrections.
4. The X—H stretching vibration is significantly anharmonic (this leads to an apparent bond length increase of ca. 0.02 Å).



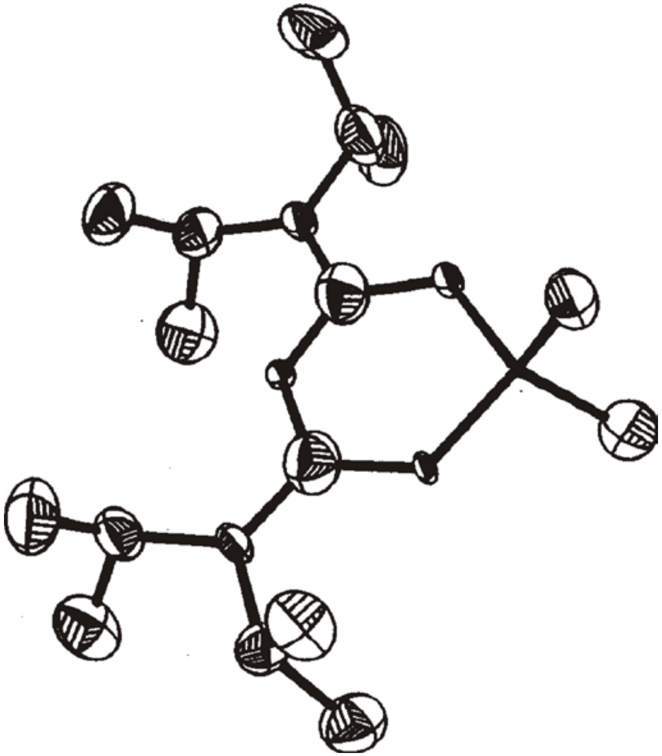
Exercises

1. A typical AsF_6^- anion showed As–F bond lengths of 1.66 Å at room temperature with the following atomic displacement parameters:

   As: U = 0.05 Å^2 in all directions;

   F: U = 0.05 Å^2 along As–F and 0.40 Å^2 at right angles to it.

   How long would the As-F bond appear to be using low-temperature data?



2. The reaction between a liquid Na/K alloy, $^{i}Pr_2NBF_2$ and 4-methyl-pyridine led to the structure shown when all atoms were refined as carbon (50% ellipsoids). The isotopic distribution in the mass spectrum indicated that there were two boron atoms in the molecule and gave a molecular weight (for the $^{11}B_2$ species) of 328. Attempt to assign the atoms!