An Unusual Molecular Deformation by Crystal Forces

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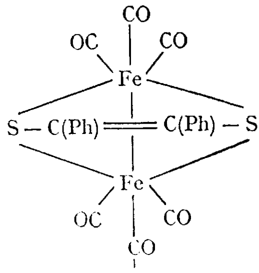
THE extent to which the crystalline environment may be responsible for changes in molecular shape and geometry is of great importance since the results of crystal structure analyses are often used, sometimes uncritically, in proposing models for more complex systems. The cardinal principle is held to be that a molecule may deform by changes in bond angles or in torsion angles so as to avoid too-close approaches between nonbonded atoms either within or between individual molecules in the crystal structure. So general is this observation that van der Waals contacts shorter than the standard values usually signal a wrong solution to the crystal structure.

We report a striking violation of this rule encountered in the crystal structure of $[PhCSFe(CO)_3]_2$ (I), which provides dramatic proof that in the interest of achieving a minimum energy for the whole lattice several highly unfavourable intramolecular van der Waals interactions can be tolerated.

$[PhCSFe(CO)_3]_2$ is triclinic; the axes chosen $a = 35{\cdot}68$, $b = 9{\cdot}30$, $c = 28{\cdot}39$ Å; $\alpha = 90°15'$, $\beta = 108°43'$, $\gamma = 103°20'$, correspond to a face-centred cell. The space group is $F\bar{1}$ with two molecules in the asymmetric unit. The analysis of the structure was carried out with over 2200 structure amplitudes. Refinement was by a combination of full-matrix and diagonal least-squares. The final value of R was 0·07.

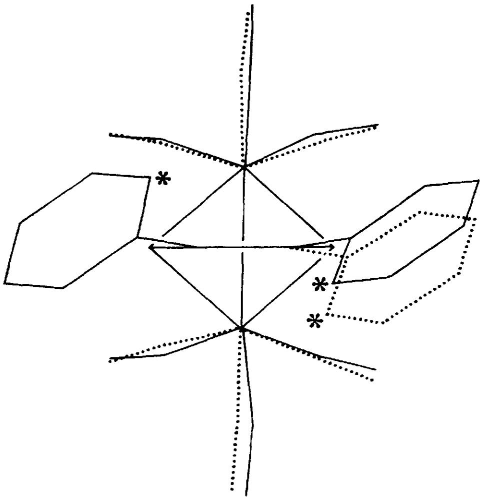
If the conformations for the two chemically equivalent but crystallographically independent molecules in the asymmetric unit are compared by superimposing them on the common base of the iron and sulphur atoms, as in the Figure, it is seen that both molecules are distorted by torsional deformation about the bridging ethylenic double bond, *but each is deformed in a different way.*



(I)

Each C–C_{phenyl} bond is twisted by about 6° out of the expected plane giving rise to a *syn*-conformation in the one case and an *anti*-conformation in the other, producing different molecular shapes.

The deformation of an isolated molecule to the *anti*-conformation may be calculated to involve between 1 and 2 kcal. mole^{-1} if the assumption is made that the torsional deformation constant is similar to that for ethylene, about $5{\cdot}10^{-12}$erg rad.$^{-2}$ This seems a reasonable supposition since the distortion serves to reduce van der Waals repulsions



FIGURE

A superposition of the two observed molecular conformations on their common $(FeS)_2$ *nuclei. The overlap between the phenyl groups on the left hand side is exact.*

between the phenyl groups, the critical distance between the asterisked atoms being 3·41 Å, a normal separation. This conformation with C_2 symmetry is undoubtedly very close to the ground state for the isolated molecule.

The deformation of the molecule to the *syn*-conformation, however, must require a very much higher energy since it leads to some very unfavourable interactions between non-bonded atoms. Thus, the distance between the asterisked atoms in this conformation is reduced to 3·17 Å and two other phenyl–phenyl contacts which are normal in the other conformation are reduced to 3·28 and 3·29 Å in this. Such strain would clearly be intolerable in the isolated molecule and must be induced so as to achieve a better overall minimisation of the lattice energy. We thus have a definite case where crystal forces produce a molecular distortion leading to substantially reduced van der Waals separations and an increase in the ground-state energy of the molecule.

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