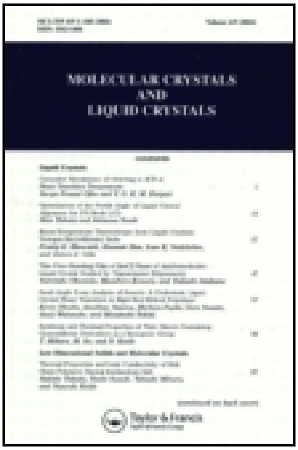

Molecular Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl15

Diffraction Studies of the Chemical Bond

Philip Coppens [a]
[a] Chemistry Department, Brookhaven National Laboratory, Upton, New York, 11973

Version of record first published: 21 Mar 2007.

To cite this article: Philip Coppens (1969): Diffraction Studies of the Chemical Bond, Molecular Crystals, 9:1, 25-33

To link to this article: http://dx.doi.org/10.1080/15421406908082731

3

Diffraction Studies of the Chemical Bond[‡]

PHILIP COPPENS

Chemistry Department,
Brookhaven National Laboratory,
Upton, New York 11973

Abstract—A number of accurate diffraction studies are discussed which have yielded information of theoretical chemical interest. The information is twofold: accurate atomic parameters can be obtained and compared with theoretical calculations through bond length-bond order curves and through analysis of molecular geometry. In addition, more direct information on chemical bonding can be obtained from combined X-ray and neutron diffraction analyses. The experimental charge density obtained in this way can be compared with theory without use of empirical correlation curves. It is concluded that accurate diffraction data have a potential for the study of chemical bonding which is as yet largely unexplored.

Introduction

In the last few years considerable advances have been made both in the collection and processing of diffraction data. With automatic diffractometers it is now possible to collect routinely several symmetry equivalent sets of intensities of crystals of small molecules. An accuracy of five per cent or less in the intensities can be obtained. Data processing techniques have been improved by allowing for effects such as absorption, extinction and multiple reflection. This improvement in accuracy has greatly enlarged the amount of information of theoretical-chemical interest that can be obtained from diffraction studies. In this paper we shall first give some examples of information which can be obtained from molecular geometry and then discuss the direct determination of electron density distribution in small organic molecules.

[‡] Research carried out at Brookhaven National Laboratory under contract with the U.S. Atomic Energy Commission.

Determination of Molecular Geometry

X-ray crystallographers have for many years provided a check of theoretical calculations by relating experimental bond lengths with bond orders with the aid of empirical curves. This method has been quite successful for series of compounds such as the hydrocarbons, in which reasonable agreement with theory was obtained, though short bonds were observed to be generally shorter than predicted.[1] Dewar and Gleicher[2] have done some more advanced MO calculations for a number of non-alternant hydrocarbons for which the Hückel theory is unsatisfactory. The molecular structure of heptafulvalene (Fig. 1) has been determined recently to an accuracy of about 0.003Å in the bonds lengths.[3] In Table 1 experimental bond lengths are compared with theoretical values given by Dewar and Gleicher and calculated with the SPO (split *p*-orbital) and PPP (Pariser, Pople, Parr) methods. The agreement is fairly good: the alternation of almost single and almost double bonds in the ring is correctly predicted by both calculations. The largest differences are 0.017Å for the C_4—C_5 bond (PPP) and 0.022Å for C_3—C_4 (SPO), of about the same size as the largest discrepancies in the compounds summarized by Trotter.[1] Generally the calculated bond lengths are too small in the center of the molecule and too large at the extremes. As in the alternant hydrocarbons surveyed by Trotter, the largest

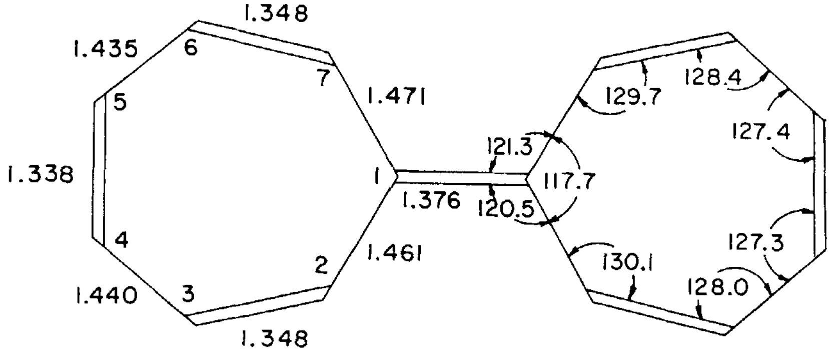

Figure 1. Experimental bond lengths (Å) and bond angles (°) in heptafulvalene. The two rings are related by a crystallographic center of symmetry. Bond lengths are corrected for apparent shortening caused by rigid body thermal motion.

discrepancy for the PPP bond lengths occurs in the shortest bond, the theoretical value being too large. This is not true for the SPO results. However, the rms discrepancy between the observed and calculated values is larger for the SPO method (0.012_5 Å as against 0.010_8 Å for PPP). It should be noted that these discrepancies are well outside the experimental errors. It is true that the effect of charge asymmetry on atomic positions discussed in the next section of this paper may have caused a decrease in the observed values for the cyclic bond lengths, but this decrease is almost certainly small compared with the discrepancy between theory and experiment.

Table 1 Comparison of Observed and Calculated Bond Lengths (Å) in heptafulvalene.
The values observed for chemically equivalent bonds have been averaged.

Bond	Observed[3]	Calculated[2]	
		PPP	SPO
C_1—C_1	1.376	1.368	1.359
C_1—C_2	1.466	1.453	1.462
C_2—C_3	1.348	1.354	1.350
C_3—C_4	1.437	1.449	1.459
C_4—C_5	1.338	1.355	1.350

The seven-membered ring in heptafulvalene provides an additional indirect test of the calculations. The ring is severely strained and the molecule is therefore not completely planar. An angle of torsion can be defined for any bond as the dihedral angle between the two

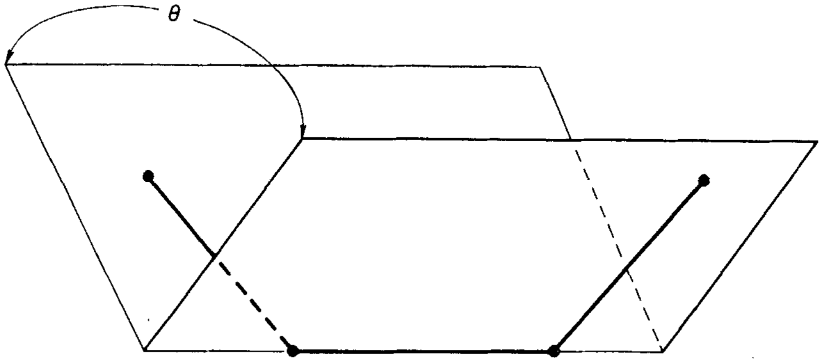

Figure 2. Definition of the angle of twist θ.

planes through the bond and each of the adjacent C—C bonds (Fig. 2, compare ref. 4). It is reasonable to assume that the molecular strain will be relieved at the bonds with the lowest bond order because the torsion of the bond decreases the overlap between the carbon π orbital and therefore the exchange integral between these orbitals. Figure 3 shows that there is indeed a correlation between angle of twist and the calculated bond order. In the next section of this paper we shall indicate how diffraction methods offer the possibility of direct measurement of bond order in light-atom molecules.

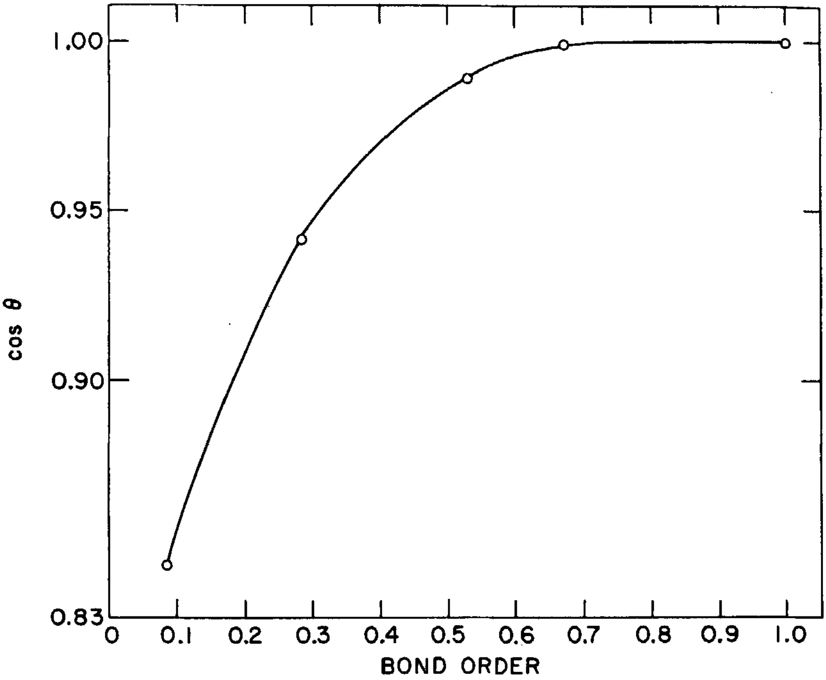

Figure 3. Correlation between experimental values of cos θ and calculated bond orders (PPP).

An example of theoretical information that can be obtained from accurate neutron diffraction studies is provided by the two polymorphs of deutero-oxalic acid dideuterate.[5] The existence of a β form of deutero-oxalic acid dideuterate (to be called β-DOX) was first reported by Fukushima, Iwasaki and Saito[6] who also did an X-ray analysis and a two-dimensional neutron study of this modification.[7] These studies indicate that the angle in the water molecule of β-DOX is larger than the angle in α-DOX. The later and more accurate determinations confirm the difference to be significant, though smaller than found initially, the angles being 108.7 ± 0.3° and 105.6 ± 0.3° in the β and α polymorphs respectively. The arrangement of the hydrogen bonds around the water molecule is different in the two structures. In β-DOX the two deuterons of the water molecule and the deuteron forming a hydrogen bond to the back of the molecule are almost coplanar with the oxygen atom, and quite different from the arrangement of the same atoms in the α structure (Fig. 4). In fact, the water molecule in the former compound is of

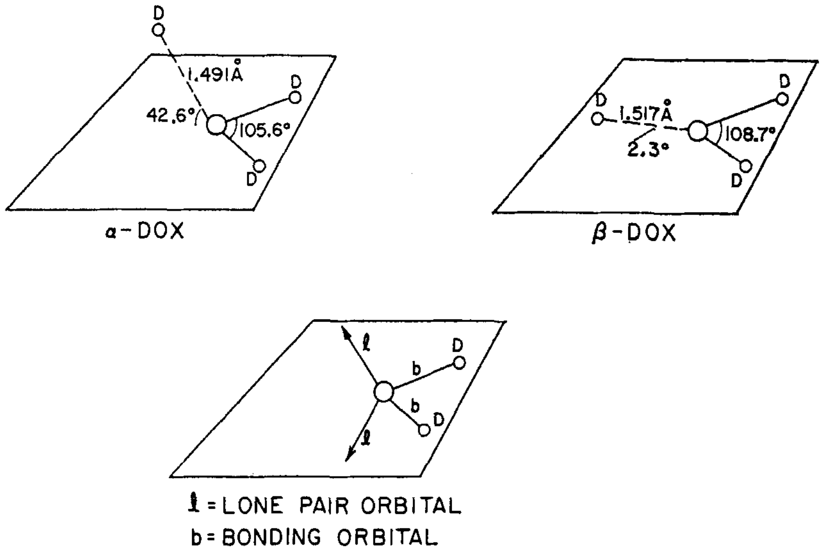

Figure 4. The configuration of the water molecules in α- and β-deutero-oxalic acid.

type *K* of the classification of Chidambaram *et al.*[8] in which one of the lone pair orbitals is directed towards an H donor group, while the water molecule in the latter structure is of the type *F* in which the bisector of the lone pairs is directed toward an H bond donor group. It is a reasonable assumption that in type *F* systems the angle between the lone pairs is decreased in order to increase the total interaction of the negative charge with the proton or deuteron of the donor group. In the orthogonal atomic hybrid approximation[9] this implies that the *p*-character of the lone pairs and therefore the *s*-character of the oxygen bonding orbitals increases. This increase in *s*-character of the bonding orbitals manifests itself in the opening up of the DOD angle. The DO bonds will as a result be slightly stronger in β-DOX. The observed bond lengths in this compound are 0.948 ± 0.003 and 0.951 ± 0.003 Å, while the corresponding values for the other polymorph are 0.955 ± 0.003 and 0.956 ± 0.003 Å. The differences are indeed in the right direction and observed for both bonds. Examination of the standard deviations shows, however, that the differences are barely significant. It is obvious that much is to be gained from a further increase in accuracy of experimental bond lengths.

Determination of the Charge Distribution

X-rays are scattered by the electrons and any determination of atomic position with X-ray diffraction is therefore indirect and dependent on assumptions, such as that the center of gravity of the electronic charge density coincides with the nuclear position. The charge distribution is in fact at least as important for the understanding of molecular structure as the nuclear configuration, but it has to be determined with great accuracy for this purpose. It appeared for a long time that the charge distribution in molecules deviated only slightly from a superposition of spherically symmetric atoms. Refinement of X-ray data has therefore been based almost exclusively on a spherical atom model. It has now become apparent that the use of such an incorrect model introduces small shifts in atomic positions (maximally about 0.01 Å and often less, depending on data cut-off and asymmetry of the environment) and somewhat larger shifts in thermal parameters derived from X-ray data.[10,11] These shifts (ca 10% of the thermal parameters for a typical organic structure at room temperature) have the effect of minimizing the apparent difference between the true electron distribution and the one obtained by a superposition of spherical atoms.

Neutrons are scattered by atomic nuclei and neutron diffraction results are therefore not subject to these errors. When a structure has been determined by a neutron diffraction experiment at the same temperature, it is possible to demonstrate bonding effects clearly.

In Fig. 5 the deviations from spherical atomic symmetry in the molecule of *s*-triazine are depicted. These density maps were obtained by subtracting from the electron density as derived from the X-ray observations the density calculated with the neutron

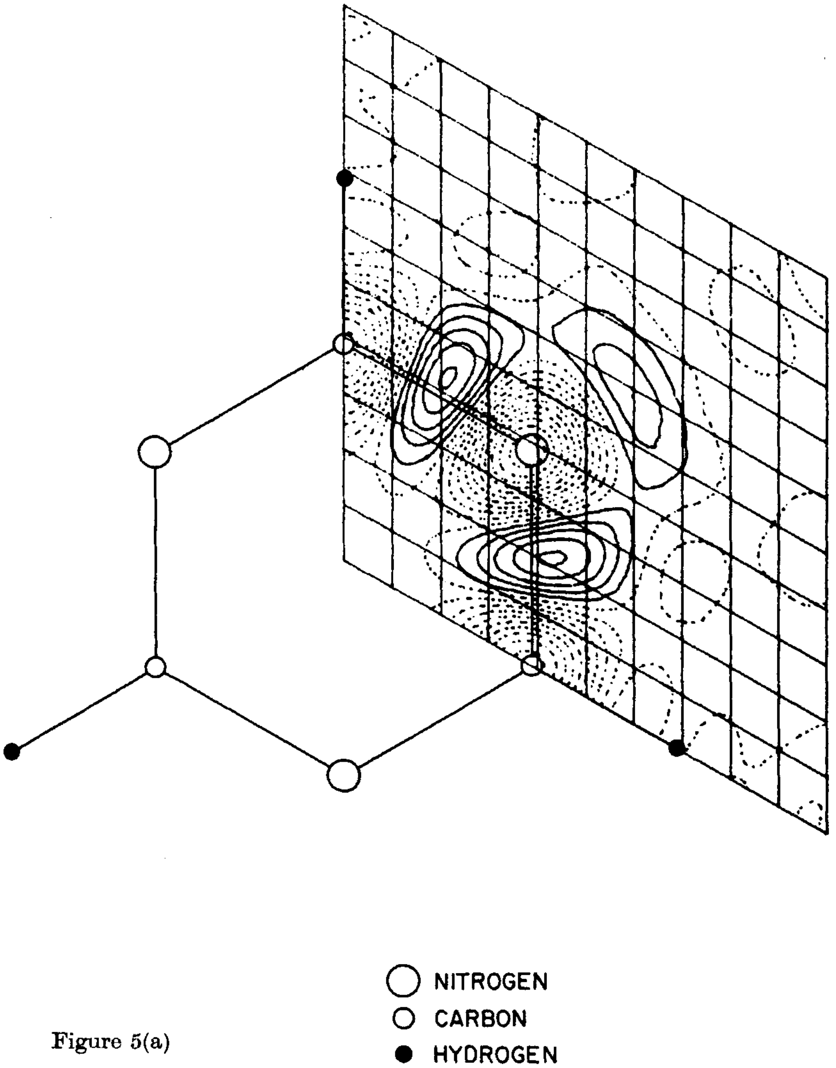

Figure 5(a)

Figure 5. X–N difference maps for *s*-triazine. Contours at 0.05 eÅ^{-3}, zero contour and negative contours dotted.

(a) section through the molecular plane.

parameters and spherically symmetric form factors. Large peaks are found in the section through the molecular plane (Fig. 5a). Compared with the spherical atom, model density has migrated from the atoms into the C—N bond and into the lone-pair region of the nitrogen atom. Figure 5b is a section through the midpoint of the C—N bond perpendicular to the molecular plane. It shows that the bond peak is more extended perpendicular to the plane than in the plane of the molecule, as is to be expected for a bond which is part of an aromatic system. Such features, which were also observed in the combined X-ray and neutron diffraction study of deutero-oxalic acid dideuterate[12] demonstrate the possibility of a direct measurement of bond strength by diffraction methods. This may be done by electron counts in density maps like the ones in Fig. 5. A probably preferable alter-

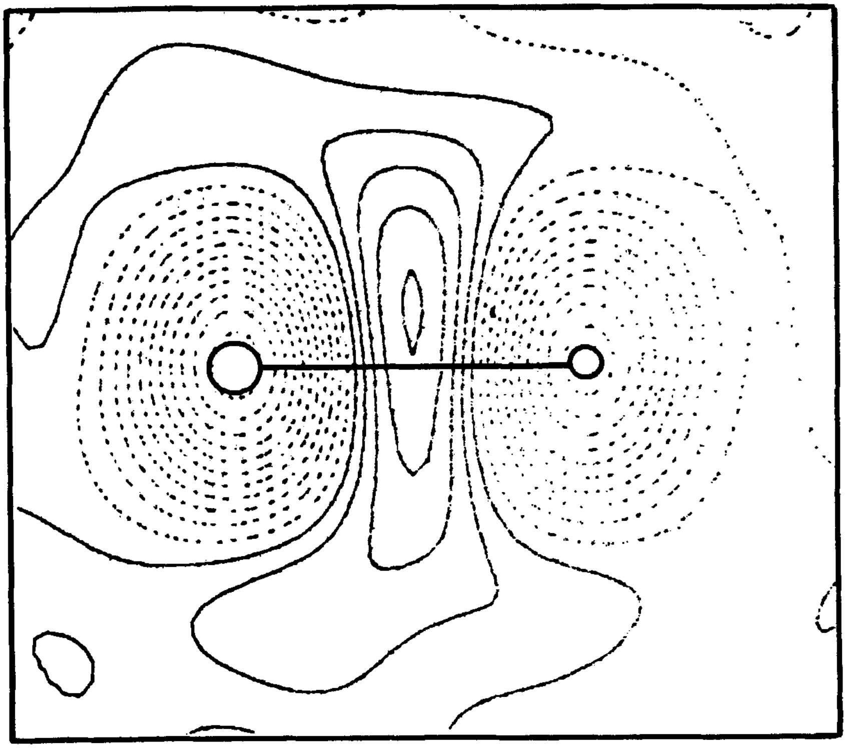

Figure 5(b)

(b) section through the C—N bond perpendicular to the molecular plane.

native is to base refinement of X-ray intensities on a model which explicitly allows for the bond overlap population and lone pair charge. With such a model one may refine parameters such as occupancy factors of localized molecular orbitals and orbital exponents, which are directly comparable with the corresponding theoretical values.

Studies of this kind can reveal whether the discrepancies for the short C—C bonds in hydrocarbons to which we referred earlier are due to an incorrect bond length-bond order relation or to deficiencies in the theoretical calculations.

Conclusion

With increased experimental accuracy and improvements in data processing, diffraction methods are becoming much more powerful. A detailed study of the chemical bond in crystals is now possible and an increasing number of such studies will become available. Molecules can be analyzed in different environments such as provided by polymorphs and mixed crystals and it is believed that the information to be obtained will contribute considerably to the understanding of the reactivity of molecules in organic solids.

REFERENCES

1. Trotter, J., *Proc. Roy. Soc.* **A289**, 366 (1966); Roy. Inst. Chemistry Lecture Series 2 (1964).
2. Dewar, M. J. S. and Gleicher, G. J., *JACS* **87**, 685 (1965).
3. Thomas, R. and Coppens, P., to be published.
4. Hirshfeld, F. L., *J. Chem. Soc.* 2126 (1963).
5. Coppens, P. and Sabine, T. M., to be published.
6. Fukushima, F., Iwasaki, H. and Saito, Y., *Acta Cryst.* **17**, 1472 (1964).
7. Iwasaki, F. and Saito, Y., *Acta Cryst.* **23**, 56 (1967).
8. Chidambaram, R., Sequeira, A. and Sikka, S. K., *J. Chem. Phys.* **41**, 3616 (1964).
9. Coulson, C. A., Valence Second Ed., p. 203, Oxford Univ. Press (1961).
10. Coppens, P. and Coulson, C. A., *Acta Cryst.* **23**, 18 (1967).
11. Coppens, P., *Science* **158**, 1577 (1967).
12. Coppens, P., Sabine, T. M., Delaplane, R. G. and Ibers, J. A., to be published.