A curiously short carbon–carbon double bond?

Jack D. Dunitz

*Organic Chemistry Laboratory, Swiss Federal Institute of Technology, ETH-Zentrum, CH-8092 Zurich, Switzerland.
E-mail: dunitz@org.chem.ethz.ch*

The discrepancy between the 'curiously short' carbon–carbon double bond distance in 3-ethynylcyclopropene, as measured experimentally by X-ray analysis [1.255(2) Å], compared with the value derived from high level *ab initio* calculations (*ca.* 1.28 Å), is largely due to neglect of corrections for molecular motion in the crystal.

The carbon–carbon double bond length in 3-ethynylcyclopropene has been described as 'curiously short' because the value 1.255(2) Å estimated from a low-temperature (120 K) X-ray crystallographic study was 'the shortest C=C double bond known in any hydrocarbon' and markedly shorter than that obtained from high-level theoretical calculations, *ca.* 1.28 Å.[1] On the basis of further, more extensive calculations, Wesolowski *et al.*[2] confirmed the validity of the discrepancy, obtaining values between 1.269 and 1.323 Å for the double bond length at different levels of theory. This apparent discordance between computational theory and experimental measurement has attracted considerable attention[3] but it probably has a simple explanation.

In 1956 Cruickshank[4] noted that rotational oscillations of molecules in crystals cause the apparent atomic positions to be slightly displaced from the true positions towards the rotation axis. This is because X-ray analysis locates the centroids of atomic distributions that are undergoing vibrations, and separations computed from these positions cannot be interpreted directly as interatomic distances.[5] Crystal structure analysis provides not only mean atomic positions but also anisotropic displacement parameters (ADPs or U_{ij} tensor components) from which principal axes and eigenvalues of the molecular libration tensor L and of the translation tensor T can be estimated together with components of a tensor S that allows for the quadratic correlation between librational and translational motion.[6,7] From the principal axis directions and mean-square librational amplitudes (eigenvectors and eigenvalues of L) approximate corrections for the shrinkage effect of the librational motion can be applied. Such corrections can easily amount to 0.025 Å.[4] In the work described in ref. 1 these corrections were not applied.

There is a problem. The *TLS* analysis can be applied only to the ADPs of the heavy atoms, here carbon. Because of the low X-ray scattering power of hydrogen atoms, their motions are usually approximated by isotropic displacement parameters and their contributions to the *TLS* analysis need to be omitted. If the five carbon atoms in the C_5H_4 molecule were exactly coplanar, the least-squares fitting of the experimental U_{ij} tensor components to the components of L would lead to a singular matrix. Indeed, the five atoms are not coplanar, but the maximum deviation from the best plane is only 0.58 Å. Moreover, as Professor H. B. Bürgi has informed us, a singular matrix also results from the condition that the atoms in the molecule lie on two mutually perpendicular lines,[8] a condition that is closely satisfied in the carbon skeleton of the C_5H_4 molecule. In addition, with only $5 \times 6 = 30$ 'observables' to be fitted to 20 tensor components, any estimate of L and hence of the shrinkage corrections must necessarily be imprecise. Nevertheless, in keeping with the low melting point (179 K), the U_{ij} values obtained in the X-ray analysis at 120 K[9] are comparable to those obtained in many room temperature analyses and are indicative of possibly large librational motions of the molecules.

Analysis of the experimental ADPs of 3-ethynylcyclopropene with the computer program THMA[10] leads to a mean-square librational amplitude of 150 deg^2 about an axis nearly orthogonal (71°) to the double bond. The resulting correction to the double bond distance is +0.022 Å, leading to a corrected bond distance of 1.278 Å, much closer to the theoretical estimates. Because of problems mentioned above, the *TLS* analysis cannot be expected to yield an accurate correction for the effect of molecular libration. Indeed, correlation coefficients among tensor components are close to unity, in accord with the expected near singularity in the least-squares matrix. However, even if the values of T, L and S given by the analysis are not uniquely determined, they represent a possible assignment among the various molecular motions that fits the experimental U_{ij} values and is also physically reasonable. Thus, the THMA analysis indicates that neglect of thermal motion is the main source of the discrepancy between the X-ray distance and the theoretical estimates.[11]

It cannot be stressed too strongly that molecular dimensions obtained by X-ray crystal structure analysis in general may be considerably in error unless corrected for the effect of molecular libration. This is apart from and in addition to any error introduced because of the inadequacy of the free-atom scattering factors for low-order reflections.

Notes and references

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6 J. D. Dunitz, V. Schomaker and K. N. Trueblood, *J. Phys. Chem.*, 1988, **92**, 856.
7 This discussion applies to rigid-body molecular motions. Complications arising from internal molecular motions are discussed by V. Schomaker and K. N. Trueblood, *Acta Crystallogr.*, 1998, **B54**, 505, but do not affect us here.
8 H.-B. Bürgi, personal communication.
9 We thank Professor Roland Boese for kindly making these available to us.
10 A FORTRAN program by the late Professor K. N. Trueblood for analysis of ADPs; available from Dr W. B. Schweizer, Organic Chemistry Laboratory, ETH-Zentrum, 8092 Zurich, Switzerland (schweizer@org.chem.ethz.ch) or Professor E. M. Maverick, Chemistry Department, UCLA, Los Angeles CA 90024, USA (maverick@chem.ucla.edu).
11 The *TLS* analysis leads to positive corrections to all the carbon–carbon bond distances in the molecule. Indeed, on the basis of Fig. 1 of ref. 2, the uncorrected experimental bond lengths all tend to be shorter than the best theoretical estimates.

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