

Citation Classics

Hughes E W. The crystal structure of melamine.
J. Amer. Chem. Soc. **63**: 1737-52, 1941.

The crystal structure of melamine was investigated by X-ray diffraction. A new method for refining atomic coordinates, based upon least-squares adjustment, was developed and used to find the positions of the atoms. The carbon-nitrogen distances in the cyanuric ring were found to be equal well within experimental error. [The SC[®] indicates that this paper was cited 637 times in the period 1961-1977.]

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"The paper covered two topics with only one mentioned in the title. The second described a new method for refining crystal structures, using the least-squares procedure. This 'hidden' part accounts for most of the citations since this method has become the standard way of refining crystal structures.

"Melamine, C₃N₃(NH₂)₃, is cyanuric triamide. It was then a rather rare chemical. I was surprised on the day that I mailed the paper to *The Journal of the American Chemical Society* to see in *Chemical and Engineering News* that 'Melamine is now available in carload lots' The principal result was that the C-N distances in the cyanuric ring are all equal, within experimental error, not alternately short and long as suggested in one earlier examination of cyanuric triazide.

"Crystal structures solved during the first decade of such work involved only one or two atoms not fixed in the crystal lattice by symmetry and the variable coordinates could easily be calculated from X-ray diffraction

amplitudes. Sir William Bragg in 1915 had pointed out the equality of the diffraction amplitudes and the Fourier coefficients for the density of scattering matter in crystals, but by 1935 no more than ten multiple-parameter structures had been determined this way, which involved evaluating two-dimensional Fourier series at hundreds of points with about a hundred terms per point. For melamine all possible two-dimensional Fourier pictures were incompletely resolved. A three-dimensional Fourier, in those days, was impossible, involving the evaluation of about a thousand trigonometric terms at about 5000 points.

"I decided to try least-squares adjustment of the atom coordinates in a two dimensional projection, although I had never then heard of least-squares problems involving so many data. A projection for melamine involves eighteen atomic coordinates. The equations connecting these with the diffraction amplitudes are trigonometric, so for linear least-squares it is necessary to linearize the equations with respect to a trial structure. It took about two eight-hour days to set up the 105 linear observational equations in 18 unknowns. With some I.B.M. bookkeeping equipment (loaned rent-free by I.B.M., to whom thanks) these were reduced to 18 'normal equations' in 18 unknowns in 4 hours. These were solved by a standard iteration method in another 4 hours.

"With the advent of electronic computers the method could be applied to three dimensional data and has become the usual way of getting optimum agreement between calculated and observed amplitudes. A modern computer would require less than a minute for one round of the 2-D melamine refinement, which in 1940 required 24 manhours of very tedious calculation. Today at least 500 structure papers per year use this method but citations are usually to published computer programs."