Acta Cryst. (1956). **9**, 233

Three Examples of Accurate Crystal-Structure Analysis by Low-Temperature X-ray Photography

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(*Received* 8 *September* 1955)

Accurate structure determinations, even by two-dimensional methods, and the approximate location of hydrogen atoms are made possible by the technique of cooling the crystals in boiling nitrogen during photography. The method is illustrated by three structures that have been refined, each in one projection, to an accuracy estimated at better than 0·005 Å in each coordinate.

In the course of our investigation of the crystal structures of overcrowded aromatic molecules (Harnik, Herbstein, Schmidt & Hirshfeld, 1954) two experimental difficulties became apparent. First, errors in measured bond lengths, especially in structures showing adjacent atoms imperfectly resolved in projection, were too large to permit definite conclusions about bond-order variations within the aromatic nucleus. Secondly, our inability to locate the hydrogen atoms prevented a complete description of the distribution of bonds about the secondary carbon atoms. Both these problems could probably have been overcome through Geiger-counter measurements of the X-ray intensities, but the experimental effort would have been considerable for unit cells of the size with which we had to deal. Alternatively, the accuracy in bond lengths might have been improved by full three-dimensional analyses, while the need for locating the hydrogen atoms could conceivably have been circumvented by the study of substituted derivatives; this would have entailed the often difficult synthesis of new compounds and their X-ray analysis.

It has been found, however, that the twofold need for accurate atomic coordinates and for the location of hydrogen atoms can be fairly satisfactorily met by the technique of cooling the crystals in a stream of boiling nitrogen during photography (Hirshfeld & Schmidt, 1954). As a result of this cooling the level of intensities reflected at high values of s ($= 2 \sin \theta/\lambda$) rises, and the range of observable reflexions is greatly extended. A low-temperature photograph of the $h0l$ zone of hexachlorobenzene, for example, shows resolved Bragg spectra out to the limit of the Mo $K\alpha$ range ($s = 2{\cdot}8$ Å^{-1}). The corresponding sharpening of the atomic electron-density maxima greatly enhances the value of two-dimensional methods of structure determination and permits accurate analyses even on the basis of quite crude photographic intensity data.

The experimental arrangement used here is indicated in Fig. 1. The wide range in $\sin \theta$ that must be recorded,

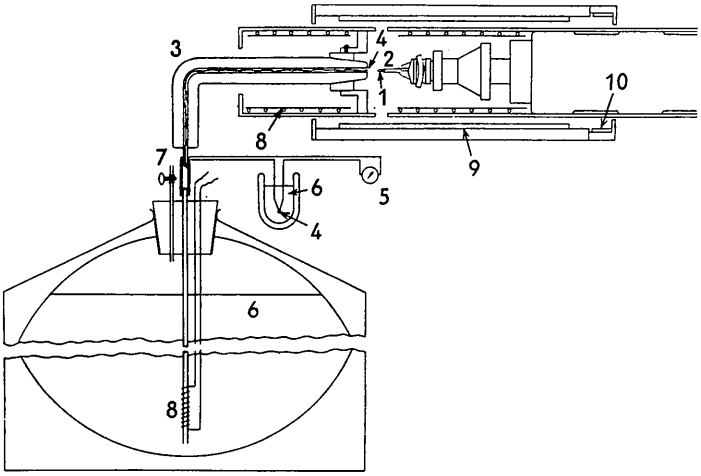


Fig. 1. Schematic diagram of low-temperature adaptation of Weissenberg camera.

1. Crystal
2. Glass capillary
3. Vacuum-jacketed glass tube
4. Thermocouple junction
5. Galvanometer
6. Liquid nitrogen
7. By-pass valve
8. Heating coil
9. Film pack
10. Film strip

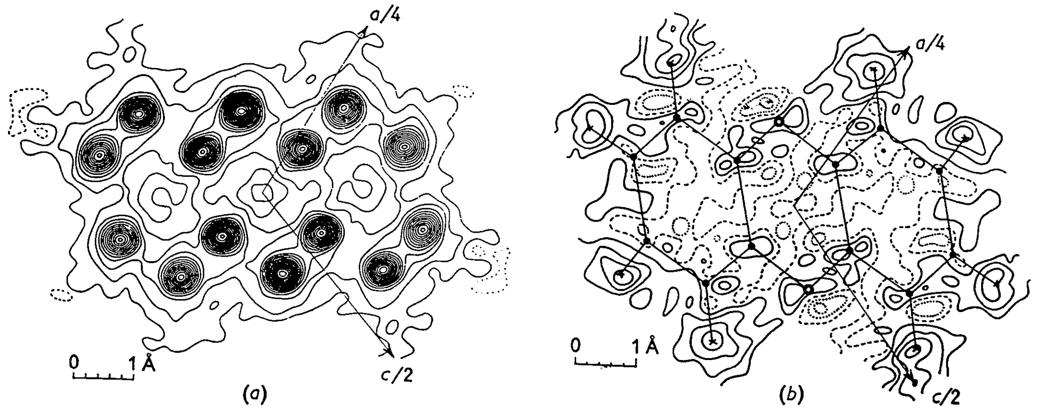


Fig. 2. α-Phenazine, b-axis projection. (a) ϱ_o contours at intervals of 1 e.Å^{-2}; zero contour broken. (b) $\varrho_o - \varrho_c$ contours at intervals of ¼ e.Å^{-2}; zero contour broken, negative contours dotted. Filled circles: C; open circles: N; crosses: H.

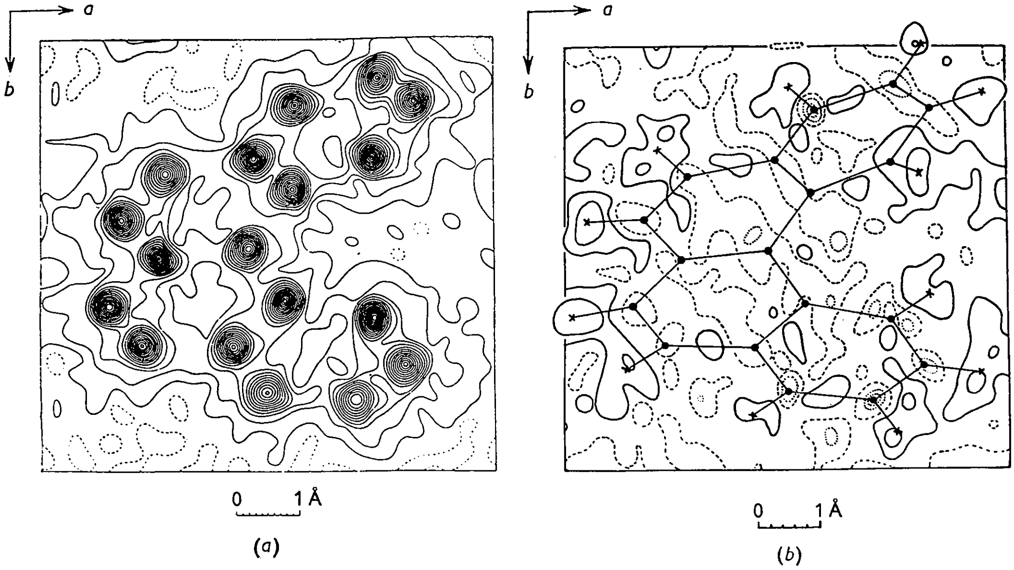
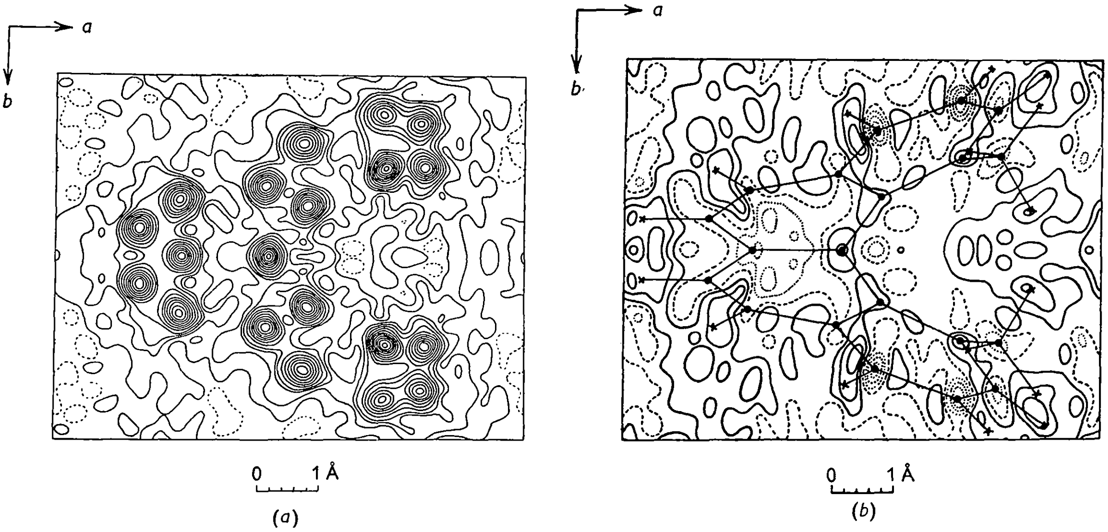


Fig. 3. 3:4-Benzophenanthrene, c-axis projection. (a) ϱ_o contours at intervals of 1 e.Å^{-2}; zero contour broken. (b) $\varrho_o - \varrho_c$ contours at intervals of ½ e.Å^{-2}; zero contour broken, negative contours dotted. Filled circles: C; crosses: H.

even with Mo radiation, precludes the use of the precession camera; accordingly we have adapted our von der Heyde Weissenberg instrument to take low-temperature photographs over a range of equi-inclination angles up to 38°. Liquid nitrogen is directed on to the crystal through a vacuum-jacketed glass tube. Its flow is regulated by the balance between the rate of boiling in the Dewar tank and the rate of escape of gaseous nitrogen through a small by-pass valve that is adjusted manually. Average consumption of liquid nitrogen is somewhat under one litre per hour. The crystal, preferably needle-shaped, is held by one end in a stout-walled glass capillary, which is securely mounted in plasticene on the goniometer head. We have encountered little difficulty with this type of mounting except that a few crystals failed to withstand the liquid-nitrogen stream, apparently because they became strained and brittle on cooling, and disintegrated after a short time. Enclosing the entire crystal in a thin-walled glass capillary was sometimes, but not always, effective in preventing such mishaps. Because of this danger it is desirable, particularly during a long exposure, to move the film holder occasionally out of the beam and to take a short photograph on a narrow strip of film so as to check that the crystal is still present, unbroken, and properly aligned.

It must be admitted that we have had considerable difficulty in photographing crystals otherwise than by rotation about their needle axes. Thus at least two structures, α-phenazine and 1:12-dimethyl 3:4-benzophenanthrene, have perforce been attacked by partial three-dimensional methods, through the use of equi-inclination photographs about their needle axes,



(a) (b)

Fig. 4. 1:12-Dimethyl 3:4-benzophenanthrene, c-axis projection. (a) ϱ_0 contours at intervals of 1 e.Å^{-2} up to 4 e.Å^{-2}, elsewhere at intervals of 2 e.Å^{-2}; zero contour broken. (b) $\varrho_0-\varrho_c$ contours at intervals of ½ e.Å^{-2}; zero contour broken, negative contours dotted. Filled circles: C; crosses: H.

Table 1. *Summary of experimental results for three structures at room temperature and in boiling nitrogen*

	α-Phenazine (*h0l*)		3 : 4-Benzophenanthrene (*hk0*)		1 : 12-Dimethyl 3 : 4-benzophenanthrene (*hk0*)	
Space group	$P2_1/a$		$P2_12_12_1$		*Pbna*	
	Room temp.	Low temp.	Room temp.	Low temp.	Room temp.	Low temp.
a (Å)	13·21	12·97	14·69	14·43	15·53	15·42
b (Å)	5·06	4·98	14·19	13·84	12·44	12·17
c (Å)	7·10	7·06	5·76	5·80	7·25	7·23
β (°)	109·3	109·0	—	—	—	—
Number of spectra recorded	106	174	154	386	119	226
Average carbon peak density (e.Å^{-2})	8·3	14·8	6·7	14·2	6·4	19·2
Discrepancy factor, excluding hydrogen	0·16	0·125	0·22	0·136	0·19	0·144
Discrepancy factor, including hydrogen	—	0·089	—	0·119	—	0·124
Estimated error of carbon coordinates (Å)	0·015	0·003	0·05	0·004	0·02	0·004

because of our inability to record the zonal reflections about other crystal axes. Repeated attempts to cut crystals of α-phenazine to shapes suitable for photography about a second axis all failed in that the cut crystals invariably broke up on cooling. Only with materials of which it was possible to produce uncut crystals of approximately cubic shape have complete structure determinations at low temperature thus far proved feasible by two-dimensional methods.

Exposure times for Cu radiation, with crystals of about 0·5 × 0·5 mm. cross-section, are about 15–30 hr.; for Mo radiation, with crystals of 0·7–1·0 mm. edge, of the order of 50–80 hr. Because of the low scattering power as well as poor film sensitivity at the Mo wavelength, the reflexions beyond the Cu range tend to be weak and therefore inaccurately estimated. Nevertheless, it is primarily these high-angle spectra whose presence at low temperature makes possible the precise location of atomic centres as well as the greatly improved resolution of neighbouring maxima in the electron-density maps.

Figs. 2–4 show the low-temperature ϱ_o and $\varrho_o-\varrho_c$ projections, down their respective short axes, of α-phenazine,* 3:4-benzophenanthrene, and 1:12-dimethyl 3:4-benzophenanthrene. The projections at room temperature corresponding to Figs. 2(*a*) and 3(*a*)

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* In a previous communication (Hirshfeld & Schmidt, 1954) a ϱ_0 projection of α-phenazine appeared with an incorrect electron-density scale. The peak densities reported there are accordingly erroneous; the correct figures are 18·4 e.Å^{-2} for nitrogen and an average of 14·8 e.Å^{-2} for the carbon atoms.

have been published elsewhere (Herbstein & Schmidt, 1952, 1954). The F_c used in the summation of $\varrho_o - \varrho_c$ did not include the hydrogen contributions.

From these maps and from the figures in Table 1 several significant conclusions emerge:

First, the sharpening of the atomic peaks at boiling-nitrogen temperature varies widely for the three structures but is in every case sufficient to bring about a very marked improvement in the accuracy of the atomic coordinates.

Second, the peripheral atoms tend to have lower peak densities than those near the molecular centres. This, as well as the asymmetry of the peaks, must be at least partly due to thermal motion of the molecules (Higgs, 1955) and suggests that considerable further sharpening should be possible at still lower temperatures.

Third, the hydrogen atoms are clearly recognizable but their positions can, in most instances, be only inaccurately inferred. They are better defined in α-phenazine, where, also, the discrepancy factor is lower, than in the other two structures. It is not certain whether this difference is primarily attributable to a difference in the accuracy of the intensity estimations or to other factors, such as the greater anisotropy of thermal motion in the two hydrocarbons.

The resolution of neighbouring atomic peaks at low temperature is illustrated in Fig. 5, which shows the effect of cooling on the electron-density distribution in a pair of atoms that were very poorly resolved at room temperature. This improved resolution, besides eliminating to a great extent the problem of peak overlap in projection, also speeds the refinement of coordinates by facilitating the interpretation of $\varrho_o - \varrho_c$ maps in terms of atomic shifts.

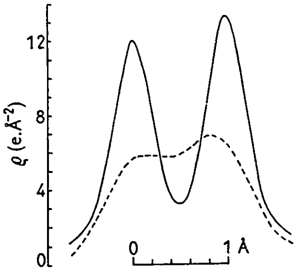

Fig. 5. Profile through C_2–C_3 bond in 3:4-benzophenanthrene c-axis projection at room temperature (broken line) and at low temperature (solid line).

No effort has been made to impose on the experimental data any particular theoretical atomic scattering-factor curves. Rather the f curves were derived as far as possible from the observed structure factors and refined along with the atomic coordinates. For each structure a single isotropic f curve was used for all carbon atoms, plus a separate nitrogen curve for phenazine; thus any differences in the shapes of the carbon atoms of a single molecule as well as any deviations from spherical symmetry are displayed directly on the final $\varrho_o - \varrho_c$ maps.

The experimental f curve for 3:4-benzophenanthrene was found to approximate to the McWeeny (1951) curve for valence-state carbon, corrected by a temperature factor of the form $\exp(-Bs^2/4)$ with $B = 1{\cdot}19$ Å^2. This temperature-corrected McWeeny curve was accordingly used for the final calculation of structure factors. For α-phenazine the experimental carbon curve (Hirshfeld & Schmidt, 1954) deviated more seriously from the theoretical curve. A McWeeny curve with $B = 1{\cdot}29$ Å^2 was found to run somewhat below the experimental curve at values of s below 0·9 and above 1·8 Å^{-1}, while running above it in the intermediate range. Most unusual was the curve obtained for 1:12-dimethyl 3:4-benzophenanthrene, which fell off much less steeply than either of the other two, approximating very roughly to a McWeeny curve with $B = 0$ at values of s up to about 0·5 Å^{-1} and thence falling off steadily to a value corresponding to $B = 1{\cdot}0$ Å^2 at $s = 2{\cdot}5$ Å^{-1}.

Our data did not permit the derivation of reliable f curves for hydrogen. However, there seemed to be a tendency in all three structures for the hydrogen atoms to scatter more strongly than would be expected even for stationary atoms in the atomic ground state. This phenomenon, which appears to be of rather general occurrence (McDonald, 1955), requires clarification.

It should be recognized that the absolute level of the structure factors and, therefore, of the electron densities, may be seriously in error inasmuch as only relative intensities were measured, the absolute scale having been estimated from the requirement that the carbon f curves extrapolate to 6 at $s = 0$.

Full descriptions of all three structures will be published shortly.

We are indebted to Prof. M. S. Newman, Ohio State University, Columbus, for samples of 3:4-benzophenanthrene and of 1:12-dimethyl 3:4-benzophenanthrene, and to Dr Fritz Klein of this Institute for his generous assistance with the design and construction of the cooling apparatus.

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