948. *The Structure of Molecular Compounds. Part XI.* Crystal Structure of the Addition Complex of Quinol and Methyl Cyanide.*

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The molecular compound $3C_6H_4(OH)_2,M$ ($M = CH_3{\cdot}CN$) has a hexagonal structure closely related to that of the other members of the series ($M = SO_2$, A, etc.) but the β-quinol framework which encloses M is distorted more than in any other known member of the series. This distortion probably includes both slight extension and puckering of the hexagon of hydrogen bonds through which the quinol molecules are linked, and a minor departure from the rhombohedral lattice.

In Part VI [1] a survey was made of the crystal structures of the series of clathrate compounds of general formula $3C_6H_4(OH)_2,M$, where M is a molecule of dimensions which permit its enclosure in cavities between two interpenetrating giant molecules formed by quinol molecules linked through hexagons of hydrogen bonds. In the structure where M is methyl cyanide the cagework of quinol molecules was considered to be extended to its limit, since the compound decomposed noticeably in the open and methyl cyanide was the largest molecule observed to form this type of clathrate compound. The extension of the cage could be measured by the angle of tilt θ (Fig. 1) of each quinol molecule from the plane of the hydrogen-bond hexagon [which is also the (0001) plane of the hexagonal unit cell in each case]. On the assumption that the hydrogen bonds were of length 2·75 Å in each structure it was possible to calculate the angle θ independently from the *a* and *c* unit-cell dimensions, and in every case but that of the methyl cyanide compound the two values of θ so obtained were in agreement. For the methyl cyanide compound, however, θ was 47° 36′ when calculated from *a* and 49° 10′ when calculated from *c*, and this discrepancy was interpreted as indicating further distortion of the quinol cage either by extension or by puckering of the hydrogen-bond hexagons. In order to investigate this matter further, a more detailed crystallographic study has been carried out.

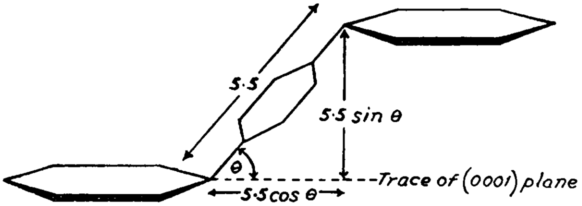

Fig. 1. *One quinol molecule is shown with its oxygen–oxygen axis inclined at an angle θ to the* (0001) *plane, together with two hexagons of hydrogen bonds parallel to this plane. Distances in* Å.

Crystals were obtained as colourless hexagonal prisms or rhombohedra by cooling warm saturated solutions of quinol in methyl cyanide. By the liquid-air method they gave a weak pyroelectric effect. On exposure to air the crystals lost methyl cyanide and by successive weighings of a sample it was found that half of the total methyl cyanide content was lost after 2½ days and three-quarters after 11 days. *X*-Ray photography of an originally single crystal of the compound showed powder lines of α-quinol appearing superposed on the single-crystal diffraction pattern as the crystal decomposed. Crystals

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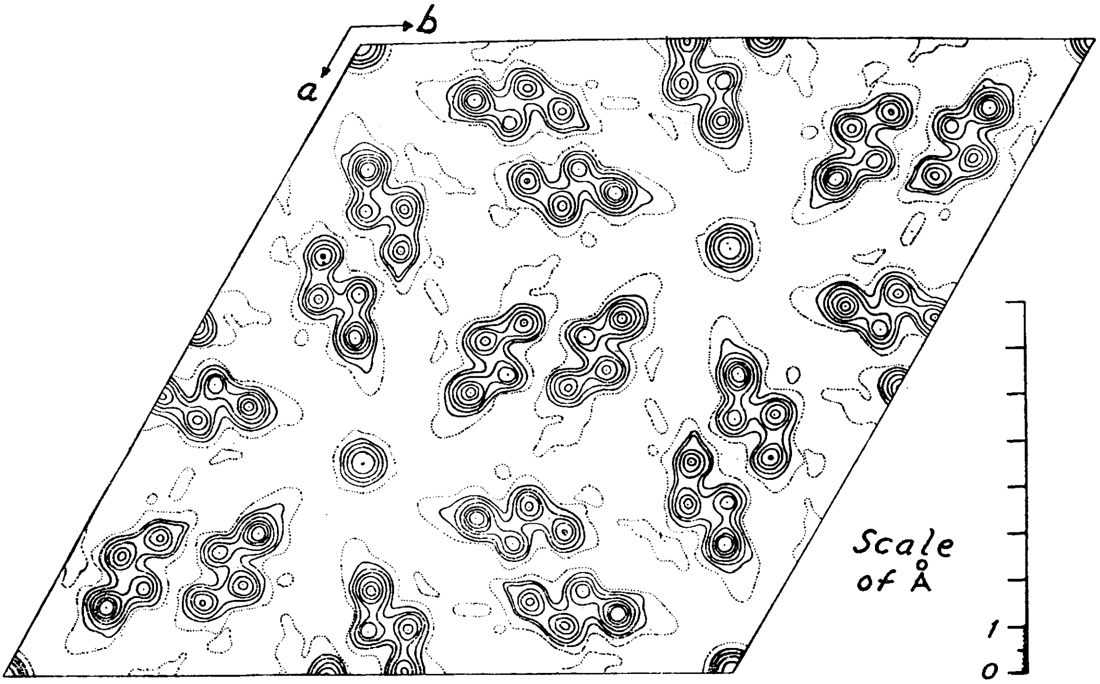
* Part X, *J.*, 1952, 319.

[1] Palin and Powell, *J.*, 1948, 815.

to be used for intensity measurements were protected by coating them with Canada balsam and these showed only slight effects of decomposition after several days. The decomposition interfered with the determination of the density by flotation in xylene–bromobenzene mixtures, but rapid determinations with fresh crystals gave approximately 1·34 g./c.c.

From oscillation and Weissenberg photographs taken with copper radiation, and with the crystal oscillating about the *a* and *c* axes of the hexagonal unit cell, the dimensions were found to be $a = 16{\cdot}01 \pm 0{\cdot}02$, $c = 6{\cdot}25 \pm 0{\cdot}01$ Å. The density, 1·34 g./c.c., and these dimensions give for the cell contents $3{\cdot}02 \simeq 3$ units of formula $3C_6H_6O_2,CH_3{\cdot}CN$. Intensities were estimated visually on long- and short-exposure Weissenberg photographs obtained by the multiple-film method.

FIG. 2. *Electron density projected on* (0001). *Lowest contour at* 2 *electrons/Å^2, others at intervals of* 1 *electron except in the methyl cyanide peaks which have contours at intervals of* 2 *electrons/Å^2. The circular peaks represent* $CH_3{\cdot}CN$ *molecules with their linear axes perpendicular to* (0001). *Each of these is surrounded by six groups of peaks representing the quinol cage. There are eight peaks in each group corresponding to the eight atoms of a quinol molecule which is tilted out of the* (0001) *plane as shown in Fig.* 1.



The diffraction patterns obtained resemble those given by the other members of the series, but differ in having some reflections for which $h - k + l \neq 3n$. These reflections are extremely weak and show that, although the structure, unlike the others, cannot as a whole be based on a rhombohedral lattice, the deviation from this is very slight. There are no systematic absences, and the symmetry of the diffraction pattern combined with the non-centrosymmetric character indicated by the pyroelectric effect show that the space group is C3.

If it is assumed that the quinol cagework has almost the same form as in the other structures of the series, and that the lack of a centre of symmetry is due only to the presence of non-centrosymmetric methyl cyanide molecules, Fourier refinement of the structure may be attempted by giving positive or negative signs rather than phase angles to F_{hki0} because the methyl cyanide molecules are seen end-on in projection along the *c* axis. A similar procedure had proved successful for the methanol compound.[2] Many signs were found by the isomorphous replacement method on the assumption that the differences in intensity of corresponding reflections in the methanol, sulphur dioxide, and methyl cyanide compounds are due mainly to the different scattering powers of the enclosed molecules (*i.e.*, the effect of distortion of the quinol cagework was neglected). In cases where no corresponding reflections had been observed for the other compounds, signs were computed from approximate parameters estimated for the atoms in the structure. In this way signs for all the $hki0$ structure factors having $h - k = 3n$ were determined and corrected by refinement of the Fourier projection on (0001).

In this projection the distortion of the structure from rhombohedral symmetry must be very slight because prolonged exposures show only five reflections having $h - k \neq 3n$. No matter what signs were assumed for these the distortion from rhombohedral symmetry of the Fourier projection was too small to be measured. In the final projection shown in Fig. 2 their signs were adjusted in such a way as to lead to equal electron densities at the positions of the methyl cyanide molecules and to the best correspondence of peak heights for similar atoms in the quinol molecules. Because the distortion from rhombohedral symmetry is too small to be measurable the atomic co-ordinates obtained from this projection and given in the Table still correspond to rhombohedral symmetry, though the co-ordinates of the full asymmetric unit of the hexagonal C3 cell are given.

The atomic positions are not expected to be more accurate than about ±0·05 Å, partly because they are all based on two-dimensional information and partly because of the difficulty of obtaining accurate intensities from crystals subject to decomposition. In view of this, although the projection is most directly interpreted as implying that the hydrogen-bond hexagons are puckered, it is not possible to rule out the alternative mode of distortion of the cagework in which the hexagons are extended but not puckered. The co-ordinates directly observed (Table) correspond to a projected hydrogen-bond length of 2·78 Å and a projected molecular length of 3·71 Å. From the latter and an assumed actual molecular length of 5·5 Å (as observed in other members of the series) the tilt θ of the molecule from the plane of the projection is calculated as 47½°. The vertical height from oxygen to oxygen is therefore 4·06 Å, 0·11 Å less than the distance between the centres of the hydrogen-bond hexagons, $2c/3$. This suggests that the hexagons are puckered so that the oxygen atoms are displaced alternately up and down from the mean plane by about 0·05 Å. In order to retain planar hexagons it is necessary to assume an error of 0·12 Å in the projected molecular length. The hydrogen bonds would then have a length of 2·84 Å. This alternative, though not ruled out, seems less probable.

Atomic x and y parameters for one asymmetric unit of the cell.

Atom	x	y	Atom	x	y	Atom	x	y
Quinol								
O_1 (OH)	0·090	0·200	C_3 (CH)	0·070	0·262	C_{11} (CH)	0·775	0·662
O_2 (OH)	0·243	0·467	C_4 (C)	0·205	0·401	C_{12} (CH)	0·930	0·738
O_3 (OH)	0·133	0·557	C_5 (CH)	0·108	0·329	C_{13} (C)	0·795	0·599
O_4 (OH)	0·910	0·800	C_6 (CH)	0·263	0·405	C_{14} (CH)	0·892	0·671
O_5 (OH)	0·757	0·533	C_7 (C)	0·067	0·529	C_{15} (CH)	0·737	0·595
O_6 (OH)	0·867	0·443	C_8 (CH)	0·995	0·554	C_{16} (C)	0·933	0·471
C_1 (C)	0·128	0·266	C_9 (CH)	0·071	0·475	C_{17} (CH)	0·005	0·446
C_2 (CH)	0·225	0·338	C_{10} (C)	0·872	0·734	C_{18} (CH)	0·929	0·525
Methyl cyanide								
C_{19} (CH_3)	0	0	C_{22} (C)	0	0	N_1 (N)	0	0
C_{20} (CH_3)	1/3	2/3	C_{23} (C)	1/3	2/3	N_2 (N)	1/3	2/3
C_{21} (CH_3)	2/3	1/3	C_{24} (C)	2/3	1/3	N_3 (N)	2/3	1/3

The calculation of the $000l$ structure factors which might distinguish between the alternative structures is complicated by their dependence on the orientations of the three methyl cyanide molecules in the cell. These are known to be aligned (at least statistically) along the c axis, and their rotation about an axis perpendicular to c is greatly hindered.[3]

[2] Palin and Powell, *J.*, 1948, 571.

[3] Dryden, *Trans. Faraday Soc.*, 1953, **49**, 1333.

It might be expected that in a succession of cavities along the *c* axis there would be a tendency for the mutual action of dipoles to align the molecules head to tail. The pyroelectric effect observed is weak and this may arise through disorder in such a column of methyl cyanide molecules, through different orientations of whole columns, or through both effects. Some diffuse reflections observed on higher layer lines but not on the zero layer line of *c* axis oscillation photographs indicate that there is disorder. The rather low heights of the Fourier peaks corresponding to methyl cyanide can be explained, as in the case of the methanol compound,[2] by the movement, with restriction, of the molecules in their cavities.

The $000l$ structure factors were calculated for a number of different structural arrangements, which involved different degrees of puckering of the hydrogen-bond hexagons and different orientations of the methyl cyanide molecules in the cell. None of the arrangements tried gave completely satisfactory agreement with the observed F_{000l} but those with puckered hydrogen-bond hexagons were more favourable than those with planar hexagons. The best agreement was obtained with puckered hexagons and with one methyl cyanide molecule in the cell pointing in the opposite direction from the other two.

With a structure of this complexity and crystals subject to decomposition and disorder, it is unlikely that the precise nature of the minor distortions of the hydrogen-bond hexagons and the departure of the quinol molecules from the ideal positions can be established without an investigation disproportionate to its importance. It seems probable that both modes of distortion, extension and puckering of the hydrogen bond hexagons, occur, the latter effect being more prominent. These distortions account for the comparative instability of this member of the series of β-quinol clathrate compounds.

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