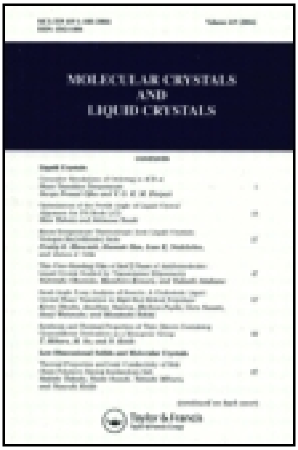

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AN INVESTIGATION INTO THE SOLID-STATE BEHAVIOUR OF ANTHRAQUINONE AND ITS DERIVATIVES

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Abstract The principle packing motif observed in anthraquinone is apparent in a number of halogenated derivatives and extends to very large polycyclic systems. Halogenation of the anthraquinone nucleus generates steric hindrance, which in extreme situations is manifested by the adoption of non-planar molecular conformations.

INTRODUCTION

Derivatives of anthraquinone (AQ) have provided a wide range of materials for the colour industry, particularly in the design of vat and disperse dyes.[1] In addition the AQ chromophore itself has also become a useful resource in the development of new colorants and is the basis of several commercial quinonoid-like systems. Consequently, a large number of anthraquinone derivatives have been synthesised.[2] For many, full crystal data has been reported in order that the intermolecular interactions responsible for the physical properties inherent to colorants may be understood.

A review by Bernstein et al [3] outlines the preferences in packing arrangements of quinonoid compounds, drawing attention to the role of C-H····O in controlling crystal packing arrangements.[4] Anthraquinone[5] itself adopts a herring-bone packing motif, as shown in Fig Ia. The space group is $P2_1/a$ with each molecule connected to four others through C-H····O hydrogen-bonds at a separation distance of 2.67 Å creating a sheet-like arrangement with hydrogen-bonding within the sheets. A similar arrangement may be seen for other heterocyclic systems, including those where N-H····O hydrogen-bonds (1.7-1.9 Å) prevail.[6]

Halogenated deriviatives of AQ and extended quinonoid systems are also of potential use. The influence of halogen substitution on the hydrogen-bond arrangement will consequently be of interest. We discuss here the effect of halogenation upon intra- and intermolecular interactions upon molecular geometry and cryssal structure. A number of crystal structures were determined to complement those available.[7]

DISCUSSION

Halogenated Derivatives

The crystal structures of 1-chloro, 1-bromo and 1-iodoAQ are isostructural and possess a similar packing motif to AQ (Fig Ib) although the number of C-H····O interactions is half that observed in the AQ. As a result, a range of hydrogen-halogen interactions (3.3-3.5Å) as well as halogen-halogen interactions (3.7-3.9Å) although C-H····O interactions continue to exist. This arrangement for monohalogenated derivatives of AQ does not appear to necessarily extend to disubstituted derivatives.

For instance, 1,5-dichloroAQ and 1,5-dibromoAQ (Fig IIa), which are isostructural, adopt a motif in which the molecular planes lie parallel promoting both C-H····O and X····X interactions. Table 1 summarises the non-bonded contacts observed in mono- and 1,5-dihalogenated species.

TABLE 1. Comparison of non-bonded contacts in halogenatedAQ derivatives

Molecule	C-H····O/Å	C-H····X/Å	X····X/Å	ref.
AQ	2.66	—	—	5
chloroAQ	2.67	3.31	3.70	8
bromoAQ	2.69	3.35	3.66	9
iodoAQ	2.70	3.51	3.85	10
1,5-dichloroAQ	2.40	3.33	3.85	11
1,5-dibromoAQ	2.44	3.41	3.69	12
1,5-diiodoAQ	2.67	3.41	3.79	12

1,5-diiodoAQ (Fig IIb) packs in a similar manner to AQ (complete with identical C-H····O separation distance) though with the hydrogen bonding now perpendicular to the molecular sheets. If iodine atoms were simply to replace bromine atoms in the 1,5-dibromoAQ structure, C-H····I and I····I non-bonded contacts would be generated at 3.32Å and 3.51Å, respectively, which are less than the sum of van der Waal's radii (vdW_{Iodine} = 2.15Å). Therefore, the molecules

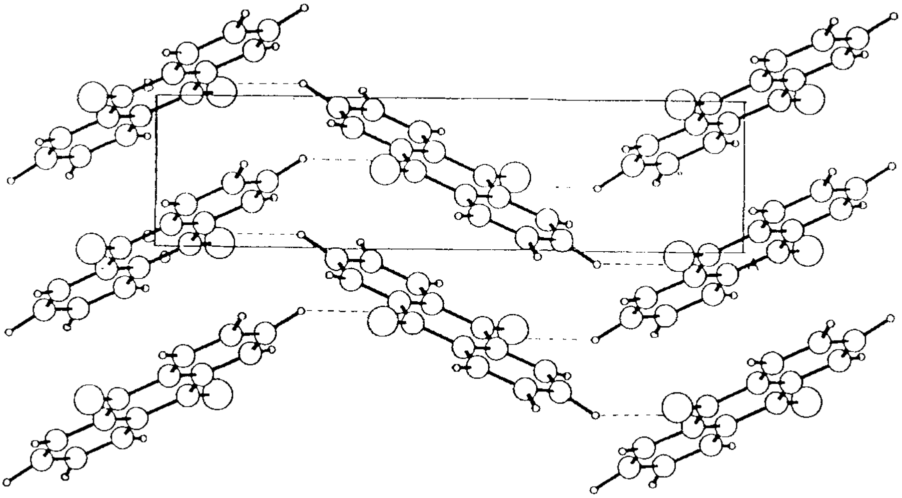


Fig Ia The packing arrangement of anthraquinone down the c-axis.

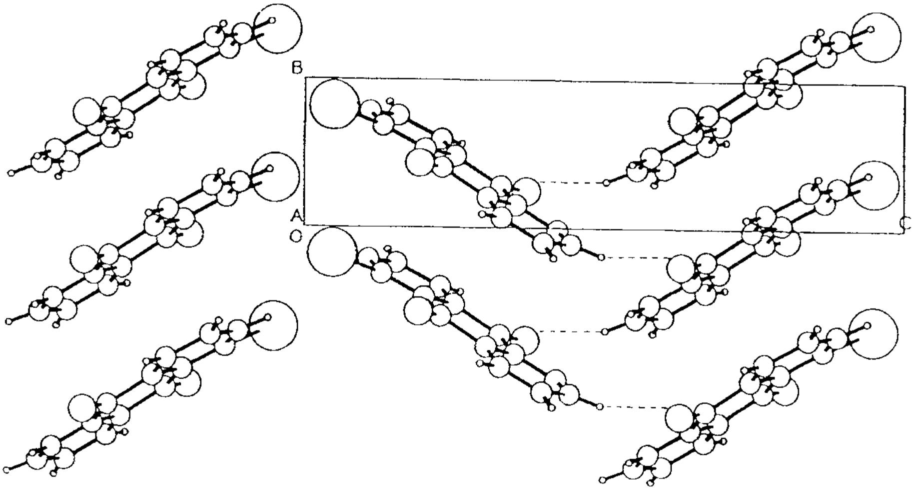


Fig Ib The isostructural packing arrangement of monohalogenated anthraquinones

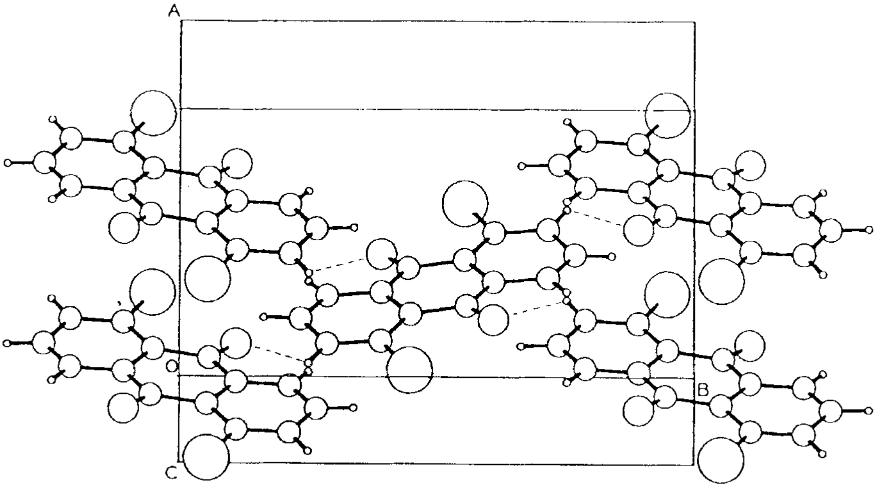


Fig IIa The parallel packing motif of 1,5-dichloro- and 1,5-dibromoanthraquinone

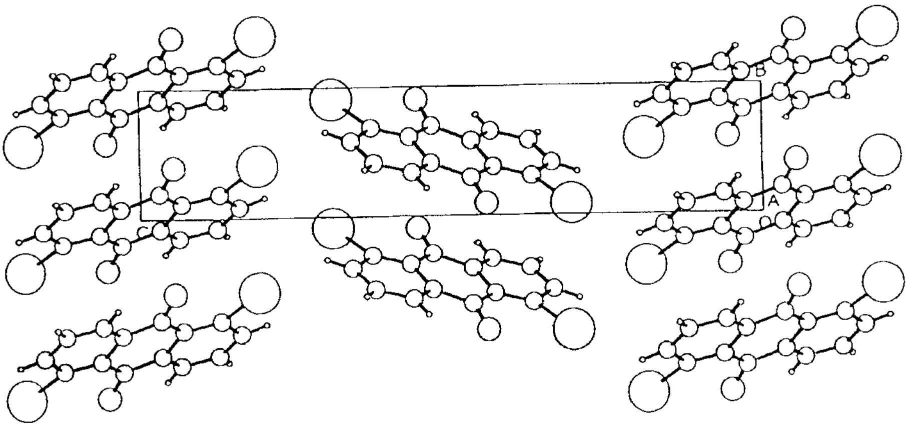


Fig IIb The packing arrangement of 1,5-diiodoanthraquione relax into the AQ packing motif and it is not surprising that some aromatic quinones,[13-14] twice the size of AQ, possess a packing arrangement identical to AQ.

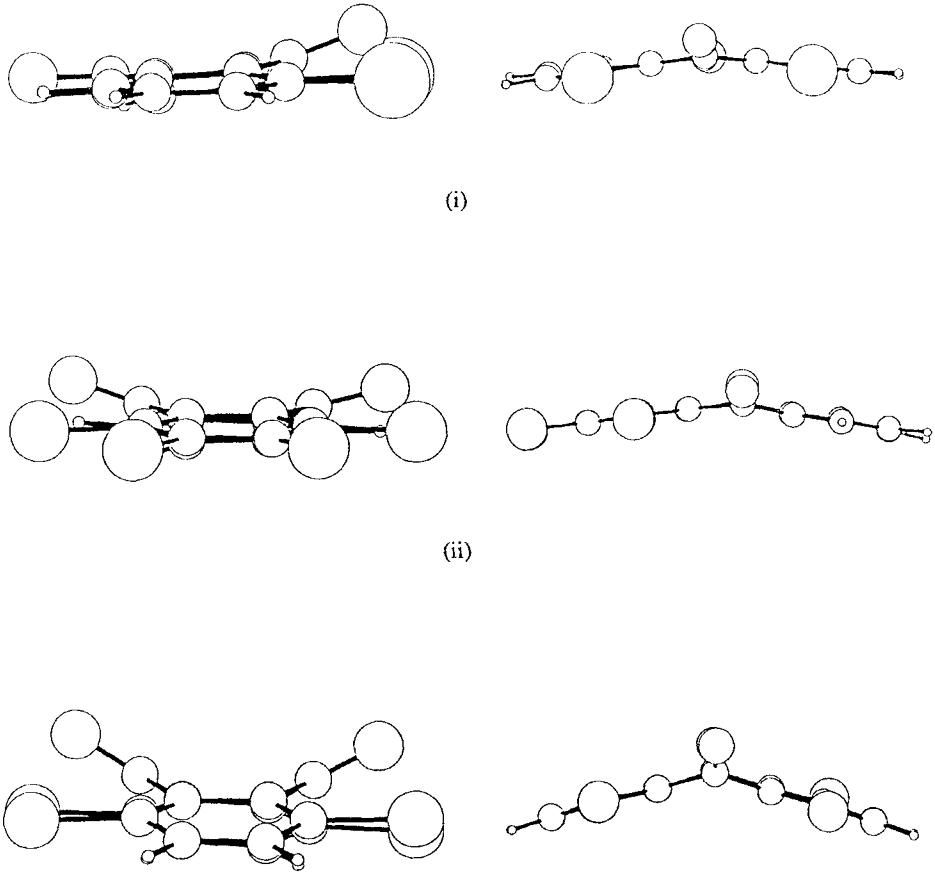
Molecular Conformation

An extension of this work considered the effect of increased halogenation upon the molecular geometry of the AQ nucleus. One of the structures reported, 1,8-dichloroAQ,[15] was found to deviate significantly from planarity. To investigate this effect further, crystal structures of other halogenated systems have been determined, see Table 2.

TABLE 2. Crystal structures investigated by geometry optimisation

Molecule	Crystal System	S.G.	R factor	Observed geometry	Calculated geometry
14DCAQ	monoclinic	$P2_1/n$	0.071	planar	planar
18DCAQ	orthorhombic	$Pca2_1$	0.157	butterfly	butterfly
148TCAQ	orthorhombic	$Pmn2_1$	0.081	butterfly	butterfly
1234TCAQ	monoclinic	$P2_1$	0.076	butterfly	planar
1458TCAQ	tetragonal	$P4_2/n$	0.083	butterfly	butterfly

Three of the four molecules were found to adopt a non-planar conformation due to pronounced intramolecular interaction between oxygen and the adjacent chlorine atoms. In each case a 'butterfly' conformation was observed (Fig III). To investigate such a possibility the structures were constructed within SYBYL[16] using the standard molecular fragments within the BUILD option. Optimisation was carried out using the third generation semi-empirical molecular orbital program MOPAC[17] employing the default minimisation criteria. The "sketched" planar molecules for 1,8-dichloro-, 1,4,8-trichloro- and 1,4,5,8-tetrachloroAQ all converged to an energy minimum with a 'butterfly' conformation. However, the optimised geometry for 1,2,3,4-tetrachloroAQ possessed a planar conformation, suggesting two possibilities; a) a local, rather than a global, minimum was reached or b) 1,2,3,4-tetrachloroAQ may exhibit conformational polymorphism. Close inspection, revealed that geometry optimisation of the experimental conformation gave a non-planar arrangement, supporting the existence of a local minimum.



(i)

(ii)

(iii)

Fig III Side and edge-on views of (i) 1,8-dichloroanthraquinone, (ii) 1,2,3,4-tetrachloroanthraquinone and (iii) 1,4,5,8-tetrachloroanthraquinone

CONCLUSION

$\pi-\pi$ stacking, between adjacent aromatic molecules, is the dominant intermolecular interaction during crystallisation, as confirmed by optical goniometry. However, the orientation of molecules, with respect to each other, is dependent upon such weak intermolecular interactions as C-H····O and C-H····X.

Steric hindrance on an isolated molecule may be sufficient to cause a deviation from planarity, however, small deviations may be an effect of temperature and insufficient data. In such cases, semi-empirical molecular orbital methods should be employed to support the experimental observations.

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