

THE SOLID STATE CHEMISTRY OF ACRIDIZINIUM SALTS

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Abstract -the crystal chemistry of various acridizinium salts (with Br, Cl, I, ClO₄, BF₄, picrate and oxalate as the counter anions) have been prepared and the X-ray structures have been determined. Despite the large movement of the acridizinium ions in the [4+4] photodimerization, the majority of these salts are able to undergo single crystal → single crystal conversion; this is especially demonstrated in the acridizinium halide salts containing water of crystallization. All the acridizinium salts described in this paper are photoreactive, the relative extent of conversion per unit time -as assessed by monitoring the loss of the IR absorption associated with the C=C bond- being I > Br > Cl > ClO₄ ≈ BF₄ ≈ Picrate ≈ Oxalate. Detailed studies of acridizinium bromide using single crystal diffractometry and powder X-ray methods, show that there are two polymorphic phases for the monomer. Preliminary evidence for the fate of the co-crystallised water during photoreaction has been obtained from differential scanning calorimetry.

Introduction

There is, at present, considerable interest in the general area of organic solid state chemistry, and in particular in the understanding of those factors which control the arrangement of molecules in a crystal lattice. More recent trends^{1,2} towards "crystal-engineering" have aimed at identifying important substituent effects which dominate the overall crystal structure. Some important interactions which have been recently investigated include chloro-chloro; carbonyl-phenyl; and sulphur-sulphur³. Strategies which have also been pursued include selective replacement of substituents by others possessing similar molecular volumes (e.g. chloro for methyl with values of 19 to 23 Å³ respectively) such that there is no

substantial change in crystal arrangement.

Also of current interest is the development and characterization of systems which are capable of reacting within the solid to complete conversion in such a manner that the final product is a single crystal of such quality that conventional structural data may be obtained^{4,5}. The ability for a reaction to proceed in this manner is important because it enables high conversions to be achieved -loss of structural integrity leads to either decreased yield or selectivity. In this context one interesting family which has been recently described is based upon 2-benzyl-5-benzylidenecyclopentanone and several of its derivatives. These compounds have been shown to undergo lattice controlled reaction in a single crystal -> single crystal manner. Furthermore, within these family the concept of structural mimicry, whereby one derivative which is inactive in its own phase is incorporated into a crystal of a reactive monomer, has also been demonstrated.

One system whose solid state reactivity has been assessed previously is based upon the crystalline acridizinium salts. Tomlinson⁶ et al. described and briefly reported upon how bromide and perchlorate acridizinium salts may show some possible application as photochromic materials -at ca. 360 nm dimerisation takes place, whereas the reaction is reversed at ca. 245 nm. We are unaware, however, of any full and detailed study on the crystal packing and reactivity of these salts as a function of the charge balancing anion.

Our own interest in these materials arose inter alia because of the possibility of extending known engineering principles to the influence of anions on crystal packing and reactivity. In this preliminary report we describe our initial findings which demonstrate that these salts exhibit interesting features of crystal chemistry including:

1. single crystal -> single crystal reactivity
2. an important role of water in modifying the course and extent of reaction
3. the movement of water molecules associated with pairs of acridizinium cations during photodimerization
4. the existence of phase transformations accompanying dimerization
5. the effect of water on modifying the packing motif of the crystal lattice and
6. the generation of crystalline solid solutions incorporating two or more anions.

Experimental

The materials were synthesized according to literature methods⁷, with the various salts prepared by standard ion-exchange methods. The acridizinium chloride salt used in this study contained approximately 15% residual bromide. Full structural details will be described elsewhere. Intensity measurements were obtained at room temperature using an Enraf-Nonius CAD-4 diffractometer. Accurate cell parameters were determined from the measurement of 25 high angle reflections. UV irradiation was at temperatures between room temperature and approximately 120 K. In certain cases the products obtained from the solid-state reaction were recrystallized for comparison with the as-prepared 'solid-state' product. A Nicolet FT-IR spectrophotometer, model MX-1, was used to monitor the extent of conversion and to study the location of water molecules within the crystal. A Perkin-Elmer DSC-1B differential scanning calorimeter was used to monitor the dehydration temperature of the acridizinium halide salts. The Rietveld program DBW-29⁸ was used to simulate the powder X-ray patterns of the different phases of acridizinium bromide hydrate.

Results and discussion

Crystallographic data for the various salts are summarised in Table 1.

Compound	monomer (M)				dimer (D)					
	M	M	D ⁺	D [!]	M	D ⁺	M	D [!]	M	M
X ⁻	Br ⁻	Br ⁻	Br ⁻	Br ⁻	I ⁻	I ⁻	ClO ₄ ⁻	ClO ₄ ⁻	BF ₄ ⁻	Picrate
n	1	1	2	2	1	1	0 4	0 4	0 4	1
Space group	P $\bar{1}$	P2 ₁ /a	P2 ₁	P2 ₁	P $\bar{1}$	P $\bar{1}$	Pbca	P $\bar{1}$	Pbca	P2 ₁
a, Å	7.525	9.996	7.737	7.741	7.632	7.938	17.458	9.116	17.047	13.220
b, Å	9.797	13.065	17.075	17.083	9.651	9.785	7.709	10.831	7.827	3.778
c, Å	9.833	10.186	9.942	9.938	10.253	9.931	17.882	13.063	17.692	19.722
α , degree	120.34	-	-	-	118.54	103.24	-	99.15	-	-
β , degree	112.41	119.10	99.15	99.25	111.33	110.33	-	98.50	-	94.69
γ , degree	72.91	-	-	-	74.01	98.96	-	105.05	-	-
Z ₀₃	2	4	2	2	2	2	8	2	8	2
V, Å ³	578.4	1162.3	1296.7	1297.2	613.2	680.2	2406.6	1205.3	2360.4	981.6
R	0.080	0.033	0.068	0.101	0.053	0.128	0.056	0.079	0.112	0.096

+ single crystal → single crystal conversion ! recrystallized from water.

The anions described are Br⁻, I⁻, ClO₄⁻, Cl⁻, picrate and oxalate. All of the

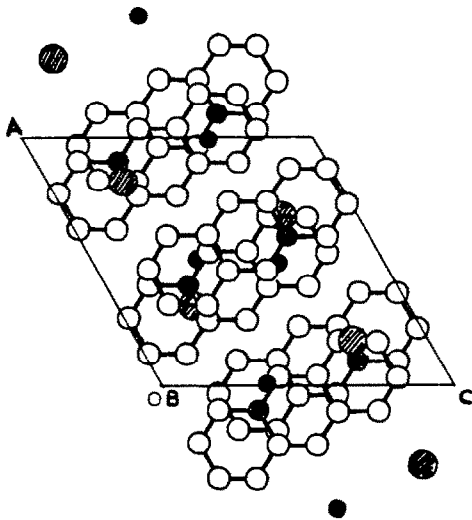
crystalline salts, although taking up significantly different overall packing arrangements, are photoactive and give dimer in high yield. Approximate values for the conversion per unit time have been obtained by monitoring the disappearance of the IR band associated with C=C at 1640cm^{-1} ; the order is $\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{ClO}_4^- \approx \text{picrate} \approx \text{oxalate}$.

Structure and reactivity of acridizinium bromide

Initial experiments⁹ suggested that the space group for this material was $\text{P}\bar{1}$ with cell parameters of $a=7.525(3)$, $b=9.797(1)$, $c=9.833(4)$ Å, $\alpha=120.34(2)$, $\beta=112.41(3)$, and $\gamma=72.91(3)^\circ$. Full structure refinement resulted in an R-factor of approximately 8%. One molecule of water of crystallization was found, with the acridizinium cations related by a centre of symmetry and the reactive centres separated by 4.3 Å. Our recent observations indicated that recrystallization from ethanol and water mixtures results in material with the same $\text{P}\bar{1}$ space group although with slightly, but significantly, different cell parameters; $a=7.511(3)$, $b=9.798(2)$, $c=9.920(4)$ Å, $\alpha=120.23(2)$, $\beta=112.21(3)$, and $\gamma=72.28(3)^\circ$. Further experiments on freshly synthesized material and recrystallization from pure water yields a structure belonging to the space group $\text{P}2_1/a$, with $a=9.996(2)$, $b=13.065(1)$, $c=10.186(2)$ Å and $\beta=119.10(2)^\circ$. This structure refined to a R-factor of 3.6% (see Figure 1).

Figure 1. Packing diagram of Acridizinium bromide viewed along [010].

- Bromine
- Oxygen
- Nitrogen
- Carbon



Single crystals of both the triclinic and monomeric phases were subsequently irradiated in situ on the X-ray diffractometer. For the monoclinic phase the product generated by photo-irradiation formed within the $\text{P}2_1$ space group, the cell parameters of the dimer as generated were $a=7.737(1)$, $b=17.075(3)$, $c=9.942(5)$ Å and

$\beta=99.15(3)^\circ$. The quality of the product was sufficient for full data to be collected and the structure refined to a R-factor of 6.8%. This was in good agreement with that found for recrystallized dimer, viz. $P2_1$; $a=7.741(3)$, $b=17.083(3)$, $c=9.938(2)$ Å and $\beta=99.25(3)^\circ$. Furthermore, when a crystal of the monomeric monoclinic form is studied as a function of conversion a gradual change in cell parameters occurs with an accompanying change in space group from $P2_1/a$ to $P2_1$. At partial conversion, however, the unit cell which is obtained is very similar to that of the triclinic structure viz. $a=7.109(14)$, $b=9.952(26)$, $c=10.151(12)$ Å, $\alpha=119.46(22)$, $\beta=110.38(13)$, and $\gamma=80.31(20)^\circ$. Irradiation of the $P\bar{1}$ monomer gave a dimer with the $P\bar{1}$ space group but slightly increased cell volume when compared with the monomer.

Role of water in the reaction

Nakanishi and co-workers¹⁰ have described the important role which water plays in the solid-state photodimerization of several cinnamic acid derivatives. In p-formyl cinnamic acid, for example, in the absence of water the product is amorphous whilst reaction in the presence of water leads to a crystalline product. We have also observed an important effect of water in the reactivity of acridizinium bromide and initial experiments on the other acridizinium halides suggest that a similar effect is also present in these solids.

In the absence of water photo-reaction stops at approximately 80% conversion. Further irradiation does not lead to any additional reaction. If the product is subsequently irradiated in the presence of water, however, the reaction goes to completion. Unlike the case of cinnamic acids, where it has not proven possible to locate the water, in this particular case because of the single-crystal \rightarrow single-crystal nature of the reaction the water may be located. One conclusion which emerges is that in both the monomer and the dimer there exist short contacts between the oxygen of the water molecule and the bromide ion. Whilst it is still not clear how the water molecules are incorporated during reaction, differential scanning calorimetry offers some useful information. The dehydration temperatures of the different acridizinium halide salts are 124, 112, and 70° respectively and decreases in the sequence of chloride, bromide and iodide. This suggests that there is a strong binding force between the water and the anion which is directly related to the size and electronegativity of the anion. In the dimer of acridizinium bromide there are two dehydration peaks, clearly showing two different

binding sites of water within the crystal lattice.

Comparison of the monomer and dimer structures

There is a clear structural relationship between the crystal packing in the monomer and dimer phases. Unlike the case of [2+2] photodimerization in 2-benzyl-5-benzylidencyclopentanone, the movement of the organic cations is quite dramatic. Viewed along an axis defined by the carbon atoms C9 and C10, photodimerization proceeds by half of each monomer moiety within the incipient dimer moving; either up or down by about 19° . The other half of the molecule remains essentially fixed (see Figure 2). There is a concomitant movement of the charge balancing anion during the photo-reaction. This movement is assumed to minimise the potential energy of the formed dimer crystal. During this movement the anion and water do not take up single well-defined sites as determined by full structure work on the bromide.

Influence of varying anion on structure

An analysis of the reactivity of several acridizinium salts is clearly of interest because of the rich variation demonstrated by these materials. A range of anions may be used as the charge balancing species, and crystal packing controlled to a certain degree by the growth of mixed anionic forms. In the case of acridizinium halides, the molecules pack in a relatively simple manner; but in the perchlorate and tetrafluoroborate salts, the presence of a tetrahedral anion results in a markedly different packing arrangements (see Figure ?).



Figure 2. Composite diagram comparing the packing of the organic components within the monomer and dimer crystal structures

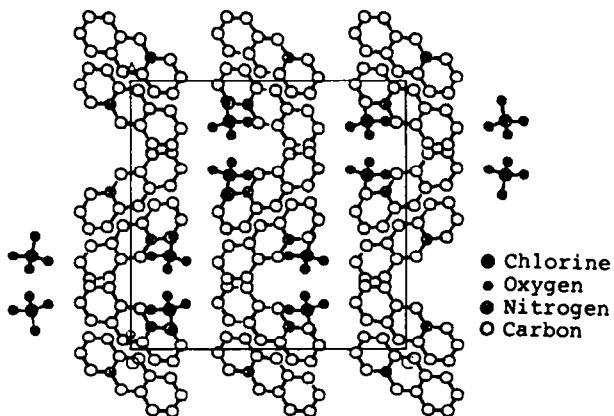


Figure 3. Packing diagram of Acridizinium perchlorate viewed along [010]

For both the perchlorate and tetrafluoroborate the space group is PbcA. A similar influence of anion-ordering has been reported by Williams and his co-workers¹¹ in superconducting materials of the general type $(\text{TMTSF})_2$. For example, the immediate nearest-neighbour environment about the disordered AsF_6^- , NO_3^- , and PO_2F_2^- reveals a nearly isotropic (symmetric) sea of H-atoms. By contrast, the tetrahedral ClO_4^- anion in $(\text{TMTSF})_2\text{ClO}_4$ possesses a very asymmetric methyl-group H-atom environment. This kind of anion-ordering has been proposed to be a necessary prerequisite to superconductivity in $(\text{TMTSF})_2\text{X}$ superconductors. This observation also explains quite reasonably why the $(\text{TMTSF})_2\text{ClO}_4$ exhibits superconductivity whilst $(\text{TMTSF})_2\text{NO}_3$ and $(\text{TMTSF})_2\text{PO}_2\text{F}_2$ do not, even under pressure at very low temperatures.

We are currently studying in greater detail the various structural features described in this paper. It is also expected that rather subtle features of chemical reactivity and structure will be revealed when the thermal or photolytic decomposition of the incorporated anions are studied.

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References

1. J.M. Thomas, S.E. Morsi, J.P. Desvergne, *Progr. Phys. Org. Chem.* 1977, **15**, 63.
2. W. Jones, J.M. Thomas, *Proc. India. Nat. Sci. Acad.* 1986, **52A**, 363.
3. V. Nalini, G.R. Desiraju, *J. Chem. Soc., Chem. Commun.* 1986, 1030.
4. H. Nakanishi, W. Jones, J.M. Thomas, *Chem. Phys. Lett.* 1980, **71**, 44.
5. H. Nakanishi, W. Jones, J.M. Thomas, M. Motevalli, M.B. Hursthouse, *J. Phys. Chem.* 1981, **85**, 8636.
6. W.J. Tomlinson, E.A. Chandross, R.L. Fork, C.A. Pryde, A.A. Lamola, *Applied Optics.* 1972, **11**, 533.
7. C.K. Bradsher, Leo E. Beavers, *J. Am. Chem. Soc.* 1955, **77**, 4812.
8. D.B. Wiles, Program for Rietveld Analysis of X-ray and Neutron Powder Diffraction Patterns: DBW 3.2, 1982, Georgia Institute of Technology, Atlanta, Georgia 30332, USA.
9. S.K. Kearsley, 1983 Ph.D. Thesis University of Cambridge, England.
10. F. Nakanishi, H. Nakanishi, T. Tasai, Y. Suzuki, M. Hasegawa, *Chem. Lett.* 1974, 525.
11. J.M. Williams, M.A. Beno, H.H. Wang, T.J. Enge, P.T. Copps, L.N. Hall, K.D. Carlson, G.W. Grabtree, *Phil. Trans. R. Soc. Lond. A*, 1985, **314**, 83.