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THE SOLID-STATE CHEMISTRY OF ACRIDIZINIUM AND 9-METHYLACRIDIZINIUM SALTS

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Abstract The photoactivity of a series of acridizinium and 9-methyl acridizinium salts is rationalised in terms of a variety of crystal packing effects. The role of ground state and excited state geometry is considered along with the molecular motion required for intermediate excimer formation. It is shown that the influence of charge-balancing anion on crystal packing is subtle and as such is an effective mode of crystal engineering.

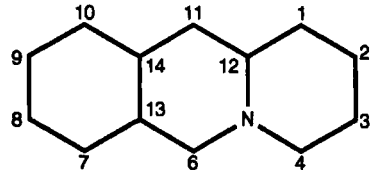
INTRODUCTION

We have previously reported upon the crystal structures of various acridizinium salts[1]. Our interest in these materials arose because of the possibility of extending known engineering principles to the influence of anions on crystal packing and reactivity as well as the development of systems which undergo single-crystal to single-crystal reaction[2,3]. They have also received attention as potential reversible photodimerisation systems[4,5]. An important modification of the structure by the anion is observed with consequential differences in reactivity[1,5]. We report here on an analysis of the factors which control the ease with which potentially reactive monomer pairs may react and in particular on the way in which the nature of the charge-balancing anion modifies the local geometry of the monomer pair.

EXPERIMENTAL

Details of the atom numbering scheme which has been used are given in Scheme 1 along with the acronyms for the various salts. Acridizinium bromide exists in two polymorphic forms - triclinic and monoclinic. The two forms are distinguished by the abbreviations ABRP$\bar{1}$ and ABRP21/a.

SCHEME 1 Acronyms for the various acridizinium and 9-methyl acridizinium salts.



A. bromide	ABRP1: ABRP21/a	A. iodide	AI
A. perchlorate	ACLO4	A. tetrafluoroborate	ABF4
A. picrate	APA	A. hexafluorophosphate	APF6
9-Me. bromide	MBR	9-Me. iodide	MI
9-Me. perchlorate	MCLO4		

A. = acridizinium: 9-Me. = 9-methylacridizinium

Initial experiments were conducted to compare the reaction of pure polycrystalline samples with that of samples when incorporated in KBr pellets suitable for infra-red analysis. Little variation was detected and as a result the reactivity data reported here are for samples prepared as KBr pellets. Samples were considered to be photoreactive if substantial changes in the IR spectrum were observed within 20 minutes of UV irradiation. Those materials considered as "stable" to UV showed no major changes for periods of irradiation up to 12 hours duration.

Relative conversion rates were obtained for the acridizinium salts by measuring the ratio of the appearance of the 1506 and 1487 cm^{-1} absorption (asymmetric and symmetric stretching frequency of -CH- in the meso position) or the 692 cm^{-1} peak in the fingerprint region in comparison with the unaffected 1456 cm^{-1} aromatic -CH- stretching overtone. For the 9-methylacridizinium salts, the corresponding bands at 1508 and 1496 cm^{-1} or 703 cm^{-1} with respect to the 1456 cm^{-1} were used. In both systems the relative peak intensities of 1637 cm^{-1} versus 1625 cm^{-1} related to the disappearance of -C=C- double bonds in the central aromatic ring were also to verify relative conversion rates. Further details have been given elsewhere[5].

RESULTS

With the exception of acridizinium hexafluorophosphate and picrate

all the crystalline salts studied are photoreactive and give dimer in high yield. The IR spectra of ABRPĪ following continuous UV irradiation (through a cupric sulphate solution and 375 nm filter) is shown in Figure 1 and illustrates the general changes which are observed following photo-reaction. Overlap of the monomers from crystallographic data is shown in Figure 2.

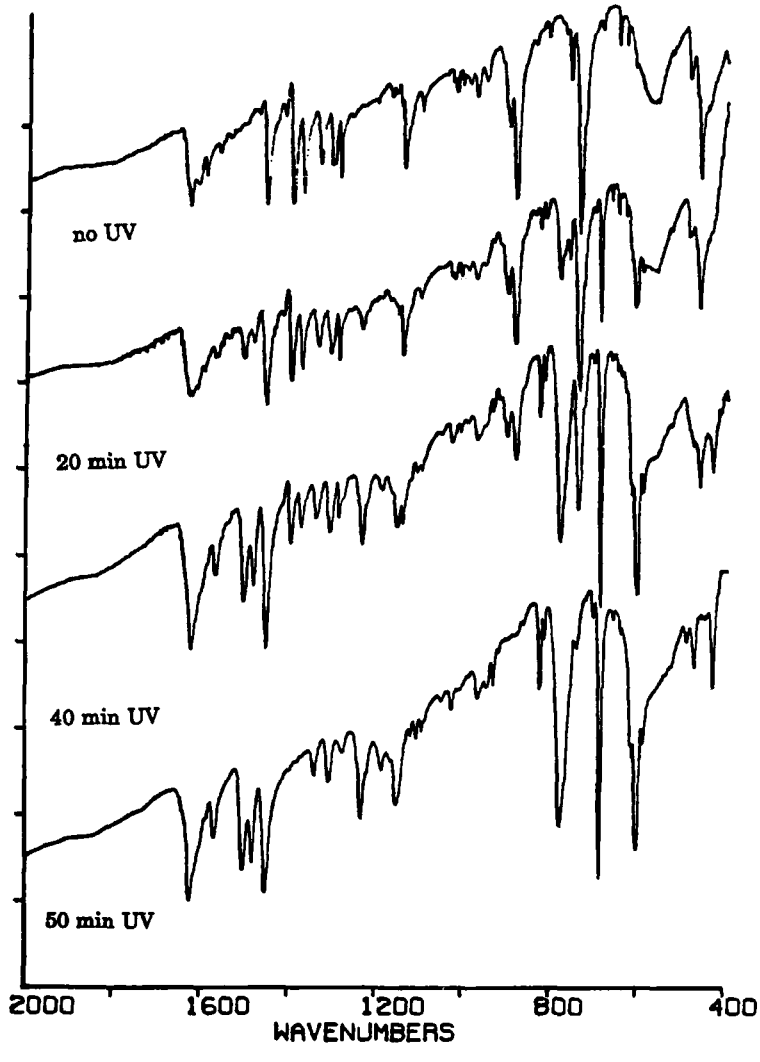


FIGURE 1 Changes in IR spectra for ABRPĪ as function of time. (Time in minutes).

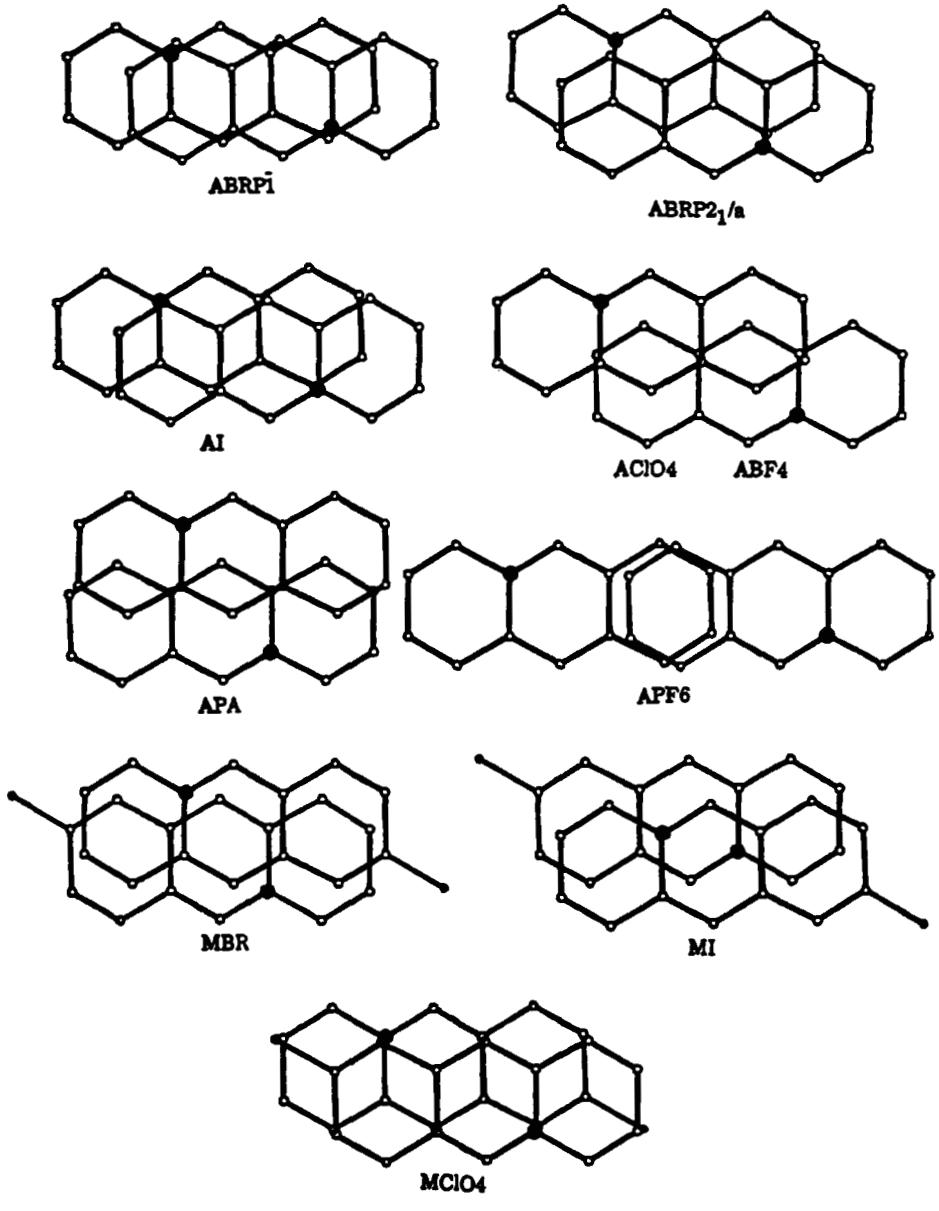


FIGURE 2 Modification of the overlap between monomer pairs resulting from variation in anion.

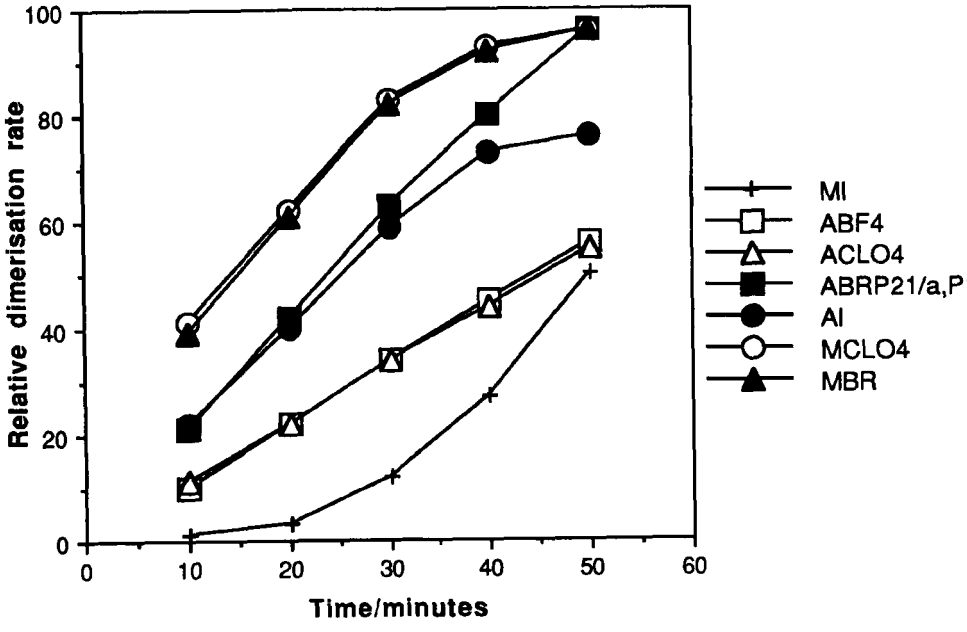


FIGURE 3 Relative rates of conversion for the various salts. (Time in minutes).

On the basis of such measurements approximate relative rates of conversion have been obtained (Figure 3). For acridizinium salts, the initial rates of conversion follow the order I ~ Br > ClO4 ~ ABF4. However, after approximately 20 minutes irradiation, the dimerization rate slows down for AI. The relative conversion rates for the two polymorphs of the bromide salt (ABRPī and ABRP21/a) are similar The overall conversion rate order is, therefore, ABRP21/a ~ ABRPī > AI > ACLO4 ~ ABF4. For 9-methylacridizinium salts there was negligible dimerization observed in the first 20 minutes of irradiation for MI and the relative conversion rates are MCLO4 ~ MBR >> MI. In all cases, a temperature dependence was observed with no reactivity detected when samples were cooled to liquid nitrogen temperatures. The reverse reaction, (i.e. monomerisation of dimer crystals) occurs at temperatures as low as 10 K[5].

DISCUSSION

1. Geometric Criteria for [4+4] Photodimerization- Ground State Considerations

Table 1 summarises the intermolecular contact angles and distances between the monomer pairs in acridizinium and methylacridizinium salts.

The distance between reacting centres is not necessarily the most important factor in permitting photochemical reaction and a more important factor may be the orientation of the participating orbital[7]. In general, the requirement for the reaction of double bonds is that the p_z orbitals associated with the reacting centres be parallel and in a near linear configuration. It is also preferable that the double bonds (sigma-bond component) be in a parallel arrangement. In solution this optimum alignment can be achieved by diffusion, whereas in a crystal lattice parallel configurations are possible through translation and inversion symmetry operations. The threshold value for maximal separation of reaction centres is considered to be around 4.2 Å. In the acridizinium and 9-methyl salts, the requirements that the reaction centres (i.e. a line joining C6 and C11) are sufficiently close as well as the p_z orbital being parallel are essentially fulfilled - see Table 1. From simple geometric criteria, therefore, spatial arguments alone would suggest that all the salts are potentially reactive.

For acridizinium perchlorate, tetrafluoroborate, picrate, and hexafluorophosphate, however, the C6-C11' contact distances are 4.26, 4.15, 4.26, and 4.26 Å respectively - close to the expected limit. Furthermore, examination of the overlap arrangement, Figure 2, indicates that there will be negligible P_z orbital overlap between monomer pairs.- yet the perchlorate and the fluoroborate react whereas the hexafluorophosphate and picrate salts are stable. Ground state considerations, therefore, do not fully explain the differences in reaction amongst the different salts.

TABLE 1 Intermolecular Contact Angles and Distances between Monomer Pairs. [In ABRP$\bar{1}$ and AI there are two potential dimer pairs - see text].

Compound	C6-C11'/(Å)	C6-C11-C6'	C11'-C6'-C11	N1-C13-C12'	C14'-C12'-C13
ABRP21/a	3.86	106.89	73.11	109.29	70.45
ABRP$\bar{1}$	3.76	103.63	76.37	74.23	105.99
ABRP$\bar{1}$	3.85	92.49	87.51	112.50	67.31
AI	3.84	105.83	74.17	71.83	108.04
AI	3.85	92.04	87.04	112.97	67.19
ACLO4	4.26	105.71	74.29	60.44	119.27
ABF4	4.15	105.85	74.15	62.99	116.83
APF6	4.26	91.75	88.25	141.13	39.38
MBR	3.66	76.67	103.33	97.82	82.51
MI	3.89	102.12	77.88	66.48	113.51
MCLO4	3.62	99.29	80.71	107.77	71.25

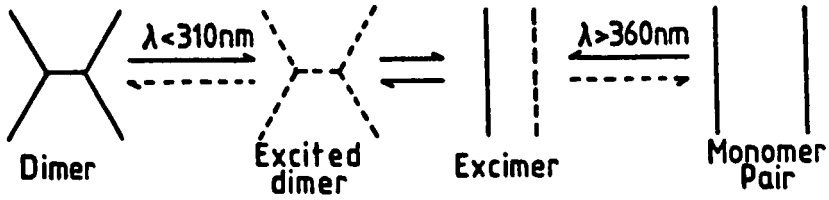
2. Arrangement of molecules in excited state

As a result of the very short lifetimes and dilution of excited molecules within the ground state matrix there is little structural information available about the geometry of the excited molecule in the solid state, although it is known that in solution excited states frequently have quite different equilibrium geometries to those of the ground state. As the molecule attains the excited state the electron density profile may change. For instance, the π^* orbital for ethene, which in the excited state contains an electron (assuming a π to π^*- transition) has a substantially different electron density distribution compared to the bonding π-orbital. As a consequence, the overlap between the anti-bonding orbital and the neighbouring ground state orbital will change (in addition to any change in the atomic geometry as a whole). Thus in the excited state arrangement overlap may increase beyond that expected from ground state geometries alone.

Tomlinson et al.[4] have shown that the sum of the quantum efficiencies

for the breaking and remaking of dimers in crystals of acridizinium toluenesulphonate is about unity, suggesting that monomerisation and dimerization go through a common excimer intermediate (Scheme 2) - a behaviour similar to that observed in the photochemistry of anthracene dimers in a rigid polymer matrix. The requirements for excimer formation prior to reaction will therefore be important in rationalising the observed differences in reactivity and variations in rate.

SCHEME 2 Schematic of the role of excimeric species in the dimerisation and monomerisation processes.



The possibility of forming excimers is particularly high for molecules which pack in planar monomer pairs - the formation of the excimer in such cases can be considered as a topochemical event. Calculations by Warshel and Huler[8]to predict the geometry of the excimeric pair of pyrene in solution and in the solid show that there is a significant change in geometry from the ground state. The plane separation in the crystal is, as in solution, about 3.2 Å. This value should be compared with the monomer pair separation within crystals of pyrene of 3.5 Å. The presence of an excimeric intermediate in acridizinium salts has been confirmed by Bendig et al.[9] with potential energy curves of the excimer showing a minimum at about 3.0 Å intermolecular distance.

(3) Thermal Assistance

Dwarkanath and Prasad[10] have established that certain organic solid state photochemical reactions are thermally assisted. Since the formation of excimer pairs does not involve either bond formation or bond breaking, the chemical potential required for this process is expected to be less than that of dimer formation. As a result excimer formation is likely to be more dependent on the rigidity of the surrounding lattice than is the situation for dimerization. The excimer configuration with minimum potential energy requires maximum overlap of molecular planes, and thus the maximum

overlap of molecular orbitals. Figure 4 illustrates the required movements to achieve the excimer configuration; movement is required both along the short and long molecular planes as well as perpendicular to the molecular plane.

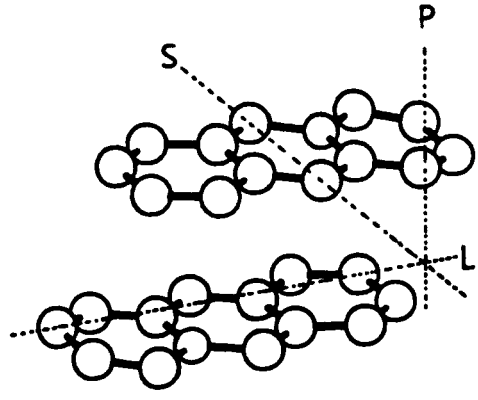


FIGURE 4 Schematic illustration of the types of motion required for conversion of the monomer pair to the intermediate excimer.

It is found that all these salts are photostable below liquid nitrogen temperature, whilst, with the exception of APF6 and APA, they are photoactive at room temperature. Thermal expansion coefficient measurements for ABRP21/a indicates that a contraction in unit cell as large as 0.2 Å along the direction perpendicular to the molecular plane can be achieved simply as a result of temperature variation. The martensitic phase transition of ABRP21/a to ABRP$\bar{1}$ by a 5 Å glide along the short molecular plane at 206 °C further illustrates that thermally assisted movement along the molecular plane is feasible[6]. Such motions are exactly those required for achieving the excimer configuration. It is understandable, therefore, why dimerisation of acridizinium salts and their 9-methyl derivatives will be thermally assisted and stop at very low temperatures. Monomerisation, however, involves bond breaking within a dimer molecule and as a result will be less dependent on temperature than dimerization.

4. Correlation of Photoreactivity with Crystal Structure

The photoreactivity of acridizinium salts can be qualitatively grouped into three categories:

(i) ABRP$\bar{1}$, ABRP21/a and AI which photodimerise comparatively fast.

(ii) ABF4 and ACLO4 photodimerise moderately fast but less than in the case

of (i).

(iii) APF6 and APA are photostable.

For the three 9-methylacridizinium salts the grouping is:

(i) MBR and MCLO4 photodimerise very fast.

(ii) MI reacts very slowly with a long induction period.

Using appropriate geometries for ground and excited state species the movements involved with excimer formation (see Figure 4) have been calculated. The required movements are given in Table 2.

For ABRP21/a, for example, excimer formation requires a 0.46 Å translational contraction perpendicular to the molecular plane (b-axis), 1.29 Å glide along the long molecular plane (c-axis), and 1.12 Å glide along the short molecular plane (a-axis). Within the crystal and relating the thickness of acridizinium cation molecule to the size of p_z orbital, then the overall thickness of the monomer pair (two acridizinium cations and two bromide-hydrate water pairs) is approximately 11 Å. The value of the b-axis of ABRP21/a is 13 Å and therefore a free space of about 2 Å along the b-axis is expected. The width of the acridizinium cation can be calculated by the bond distance and van der Waals radius of the carbon and hydrogen. The overall width (one acridizinium cation modified by adding the inclination factor and one bromide-water pair) is about 9 Å. The a-axis is approximately 10 Å and therefore a free space of about 1 Å is expected along a-axis. The overall length of the acridizinium cation is about 9.6 Å, and the c-axis about 10.2 Å with a free space, therefore, of about 0.6 Å expected.

Vibrational movement along the b-axis might, therefore, encounter less restriction as a result of the larger free space available and negligible steric hindrance to movement in this direction. For the a-axis, which has half the free space of that available along the b-axis and certain amount of steric hindrance among the hydrogen atoms attached to C2, C3, C8 and C9, movement along this direction is expected to encounter a slightly larger energy barrier. With very small free space and significantly larger steric hindrance (caused by the smaller bromide-water pair width than that of acridizinium cation), movement along the c-axis is expected to be yet more difficult. Results from thermal mechanical analysis follow these trends, with the thermal expansion coefficients being inversely proportional to the encountered energy barrier[6].

TABLE 2 Movements required in generation of excimers

Compound	Separation/ Å	P/ Å	L/ Å	S/ Å
ABRP21/a	3.46	0.46	1.29	1.12
ABRPī	3.51	0.51	1.02	0.88
ABRPī	3.55	0.55	1.48	0.17
AI	3.50	0.50	1.20	1.05
AI	3.54	0.54	1.49	0.20
ACLO4	3.52	0.52	2.10	1.15
ABF4	3.55	0.55	1.88	1.13
APF6	2.70	-0.30	3.29	0.13
MBR	3.53	0.53	0.48	0.84
MI	3.48	0.48	1.55	0.82
MCLO4	3.37	0.37	1.16	0.58

P -contraction movement along the direction perpendicular to the molecular plane, calculated by subtracting the excimer separation from the plane separation: L - gliding movement along the long molecular plane: S - gliding movement along the short molecular plane.

For all the acridizinium salts except APF6 a contraction is required for excimer formation in the direction perpendicular to the molecular plane . There is a very small energy barrier due to steric hindrance for this motion and the range of motion amongst the various salts is very small (between 0.46 and 0.55 Å). This translational contraction is not, therefore, expected to be the rate-determining step for dimerization.

For consideration of movement parallel to the molecular planes, packing features and crystal symmetry provide a good guideline for classifying photoreactivity, i.e. - space groups with only inversion (Pī), space groups with screw axis and glide symmetry ($P2_1/a$, $P2_1/n$, and Pbca) and space groups without symmetry (P1).

Both ABRPī and AI crystallise in the Pī space group, the reaction centres being related by inversion. There are two possible candidates for the excimer formation in ABRPī and AI: one pair (pair A) related by inversion and the other (pair B) related by a combination of translation and inversion operations. Structural considerations indicate that a larger energy barrier is

encountered for the gliding along the long molecular plane than that of short molecular plane. Therefore, gliding along the long molecular plane may be expected to be the rate-determining step, and the gliding distance used as an means of estimating the relative reaction rate. Approximately 1.02 (pair A) and 1.48 Å (pair B) are required in ABRP$\bar{1}$, with 1.20 (pair A) and 1.49 Å (pair B) required for AI for excimer formation. Photodimerization of ABRP$\bar{1}$ and AI is expected to occur preferentially in pair A, and the relative conversion rate slightly faster for ABRP$\bar{1}$ than for AI (despite the much shorter gliding along the short molecular plane required for pair B of ABRP$\bar{1}$ and AI (0.17 and 0.20 Å respectively) to form the excimer). Gradually the relative dimerization rate of AI decreases due to the larger gliding distance along the long molecular planes and more congestion caused by the larger size of iodide compared with bromide.

ABRP21/a also has two types of molecular pairs. One pair is related by inversion, and another pair generated by an a-glide perpendicular to the b-axis and a 2_1 screw axis along the b-axis. The dihedral angle between the molecular planes of these two pairs along the long molecular plane is less than 5°. As a result the packing arrangement of the acridizinium cations in ABRP21/a is very similar to that of ABRP$\bar{1}$. No significant steric hindrance is, therefore, expected. A 1.29 Å movement along the long molecular plane is required for excimer formation and an approximately similar conversion rate for ABRP21/a and ABRP$\bar{1}$ is then expected. This is consistent with the experimental result.

Both acridizinium perchlorate and tetrafluoroborate crystallise into the Pbca space group with glide symmetry along all three axes. This structural relationship introduces a domain boundary for the gliding movement in the edge of acridizinium cation, the perchlorate and tetrafluoroborate charge-balancing anions being present at the boundary. However, the molecular packing densities of ACLO4 and ABF4 are 0.76 and 0.73 respectively, which are lower by 0.02 to 0.04 than that found for the halides. Therefore the gliding movement along the long molecular plane is relatively restricted, with 1.88 and 2.10 Å required for ABF4 and ACLO4, respectively, for excimer formation. Considering the longer gliding distance and slightly higher energy barrier resulting form hydrogen bonding in these crystals the relative dimerization rate is expected to be slower than that for acridizinium halides - consistent with the experimental observations.

In the case of acridizinium hexafluorophosphate, the perpendicular distance (2.70 Å) within the monomer pair is shorter than that of excimer. The required translational movement perpendicular to the molecular plane for the excimer formation is thus an expansion rather than a contraction. This expansion is likely to a high energy process and coupled with the long gliding distance along the long molecular plane (3.29 Å) will prohibit photodimerization.

For all 9-methylacridizinium salts, the potentially photoreactive monomer pairs are related by inversion. The characteristic of the crystal packing in 9-methylacridizinium salts is that the charge-balancing anion tends to sit in the 9-methyl group cavity. As a result, translational glide along the long molecular plane to form the excimer is likely to encounter the highest energy barrier. This in turn will become the rate determining step for photodimerization. Both MBR and MCLO4 crystallise in the $P\bar{1}$ space group. In order to form the excimer, 0.48 and 1.16 Å movement along the long molecular plane is required for MBR and MCLO4 respectively. Unlike all other salts studied, MBR requires a longer glide movement along the short molecular plane (0.84 Å) than along the long molecular plane to form the excimer. The free space along the short molecular plane (1 Å) is only slightly longer than that of long molecular plane (1.2 Å) for MBR, a very similar energy barrier for both gliding motion is expected. An unusually small translational contraction (0.37 Å) is required to form the excimer for MCLO4 compared with that for MBR (0.53 Å). No perchlorate ion is located between two neighbouring 9-methylacridizinium cations along the short molecular plane (along line C6 and C11). Therefore, a small energy barrier may be expected for a glide along the short molecular plane. Consequently, a slightly faster conversion rate is then expected for MCLO4 than for MBR.

In the P21/n space group MI encounters a particularly large steric hindrance at the edge of the long molecular plane. Although the required gliding along the long molecular plane to form the excimer (1.55 Å) is smaller than that of ACLO4 and ABF4, the unusually large congestion at the edge of the long molecular plane caused by the combined effect of 9-methyl group cavity and the size of the iodide anion generates a domain barrier for the photodimerization. The long induction period and the slowest conversion rate of MI may result from this characteristic.

CONCLUDING REMARKS

We have considered the factors associated with the solid state dimerisation of a range of acridizinium and 9-methyl acridizinium salts. It is clear that a variety of factors are associated with the rate of dimerisation in these salts. Whilst the ground state arrangement of the molecules is important in determining the primary likelihood that reaction will occur, the nature of the excited intermediate species also plays a role. Particularly important, however, appears to be the ease with which such intermediate excimeric species may be generated. On balance, however, the overall rates with which these materials react may be rationalised. Fuller discussion of the crystal structures and the electronic factors associated with reaction will be presented elsewhere.

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