

Structure, energetics and homoaromaticity

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Abstract - A series of carbenium ion salts have been isolated as crystalline solids and their structures determined using X-ray crystallography. The cations examined include several tropylium and cyclopropenium cations, two different cyclopropyl carbinyl cations, three homotropylium cations, a bicyclo[3.1.0]hexenyl cation and several protonated benzophenones. The structures of these cations are discussed in terms of the nature of the electron delocalization which occurs in them. In particular attention is focused upon the questions of homoaromaticity and antihomoaromaticity in these cations. Conclusions reached on the basis of an analysis of structure are buttressed with some thermochemical measurements. As many of the cations studied here include a protonated carbonyl function, the structure and the charge distribution in this group is explored.

INTRODUCTION

The fundamental questions at issue in the study of carbenium ions are those concerning their structure and energy and most studies of these trivalent positively charged carbon compounds have been concerned with one or other of these questions. However, to this point in time, most of the structural information available has been obtained from indirect methods such as spectroscopy and rates of formation, rather than by more direct methods which involve the isolation of carbenium ion salts as pure materials. There is an obvious reason for this in that carbenium ions are very reactive species that present some obvious technical difficulties in handling as crystalline solids. As a consequence, there are very few reports of structure determinations using X-ray crystallography (ref. 1) or other diffraction methods. Several developments are working to change this situation at the present time. These include the experience gained in the use of super-acids and non-nucleophilic media to prepare carbenium ions in solution, advances in the techniques of handling very hydroscopic materials at low temperatures, the development of X-ray diffraction methodology, and advances in solid state NMR methods. Making full use of these developments, we have initiated a broad ranging program to determine the structures of a variety of carbenium ions.

The need for definitive structural information on carbenium ions at this time is well exemplified with the cyclic cations. Even with the aromatic cations there is a paucity of good structure determinations and before examining some homoaromatic cations it is important to know more about these conventional aromatic systems. In terms of the homoaromatic cations, for the most part the nature of the delocalization in such cations has been inferred from an examination of their ^1H NMR spectra and the seeming need to invoke an induced ring current to account for the chemical shifts of the bridging methylene protons. This almost exclusive use (abuse!) of one criterion is open to question as has been outlined in a recent review (ref. 2). For a cation to be termed aromatic or homoaromatic, a variety of different types of evidence need to be examined including particularly the molecular geometry of the species in question. It is this question which will be examined here. In the first part of the paper the structures of some aromatic cations will be examined and subsequently the discussion will be extended to some homoaromatic systems. Thermochemical measurements will be used to buttress the conclusions reached on the basis of an analysis of the structures of some of the cations.

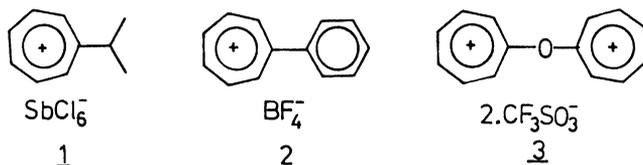
Before examining some of the structures one further general point needs to be made. In all the structures that will be discussed there do not appear to be any specific cation/anion interactions that would be expected to perturb the structure of the cation as compared to that found in solution. This is evident in the the several instances where solid state CPMAS ^{13}C NMR spectra have been obtained and shown to be directly comparable to the spectra

obtained in solution. One type of cation anion interaction which is invariably found in the protonated carbonyl compounds is a very strong hydrogen bond between the OH proton and an electronegative element in the counter ion. Such an interaction will naturally also be present in solution and thus will not alter the overall structure of the cation in the two phases. In summary, the structures that are found in the crystalline state for these carbenium ions should reflect accurately those which will be present in solution.

STRUCTURES OF SOME TROPYLIUM CATIONS

The tropylium cation was the earliest of the aromatic cations to be prepared and characterized. These cations are exceptionally stable systems that are readily isolated as solids. It is thus surprising how little structural information there is available for these 6π -electron aromatic cations. The parent ion either as a perchlorate or iodide salt undergoes rotation in the solid state and no accurate geometric parameters are available (ref. 3). In addition to some complex polycyclic systems containing a tropylium cation, the structures of acetyltropylium bromide and a mixed crystal of phenyltropylium fluoroborate-triphenylmethyl fluoride have been reported (ref. 3). Unfortunately, the errors associated with these latter two determinations are such that no meaningful internuclear distances in the seven-membered rings can be obtained.

The structures of three additional tropylium salts have now been determined in our laboratories. These cations are isopropyltropylium hexachloroantimonate, 1, Fig. 1, phenyltropylium tetrafluoroborate, 2, Fig. 2, and ditropenyliumyl ether bis(trifluoromethanesulfonate), 3, Fig. 3 (ref. 4).



In examining these structures it is clear that the presence of a substituent on the seven-membered ring has stopped the rotation that was observed in the parent cation. Both 1 and 2 have a high symmetry in the crystal lattice with 1 being on a mirror plane which runs through C_8 , C_1 and the mid point of the C_4, C_5 bond while 2 has a C_2 axis through these same positions. This symmetry in these cations means that the positions of C_4 and C_5 are coupled and not too much significance should be placed on the seeming shortness of the bond between these two atoms in 1 and 2.

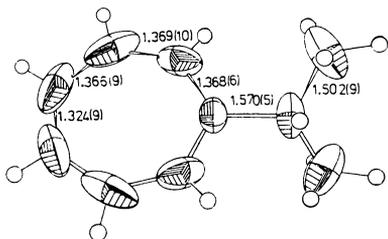


Fig. 1. The structure of 1.

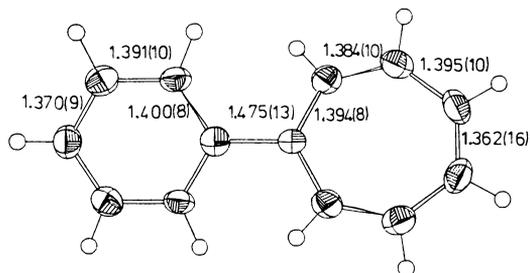


Fig. 2. The structure of 2. Twist angle between rings 29.7°

In cations 1 and 2 the seven-membered rings are planar while in 3 the rings exist as shallow boats. With the exception of the C_4, C_5 internuclear distances in 1 and 2, the bond lengths in all of the tropylium rings are the same within the error limits of the determinations. Similarly, the bond angles around the seven-membered rings are all close to the 128.6° angle expected for a regular septagon. Overall, the structures of these cations are quite consistent with them being classified as aromatic.

The average C,C bond distance observed in the tropylium rings of 1, 2 and 3 is 1.378\AA . It is worth noting that this distance is the same as or possibly somewhat shorter than that of benzene, 1.395\AA despite the formal bond order between adjacent atoms in a tropylium cation being less than that in benzene, 1.43 as compared to 1.50, respectively.

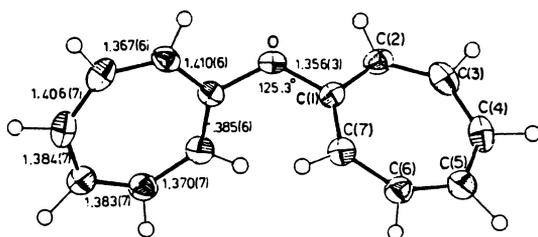
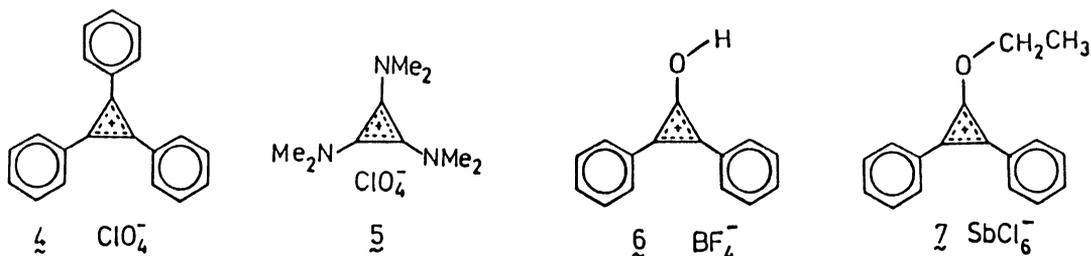


Fig. 3. The structure of 3. Each ring twisted by $33.5(5)^\circ$ from C-O-C atom plane.

The two tropylium rings in 3 are related by a C_2 axis through the oxygen atom with both rings being twisted from the C-O-C atom plane by 33.5° . While the C-O-C bond angle for 3 (125.3°) is typical of that found for a diaryl ether, this bent configuration about oxygen does not correspond to the linear arrangement predicted by Apeloig on the basis of calculations (ref. 6). While the conjugation of the two cationic rings with different lone pairs on a sp hybridized oxygen atom might be aesthetically appealing, both 3 and also two other dication ethers whose structures have been reported by Stang and Maas (ref 7) avoid this unprecedented configuration. The uniform lengths of the C,C bonds in the seven-membered rings of 3 and the relatively long C-O bond distance, $1.356(3)\text{\AA}$ (vide infra) suggest that there is no substantial involvement of the oxygen lone pairs with either of the two rings.

CYCLOPROPENIUM CATIONS

The cyclopropenium cations represent another fundamental type of aromatic system. There is more structural information available for these cations than there was for the tropylium ring, however, the two reported examples, 4 and 5, of 'simple' cyclopropenium cations in each case bear three identical substituents which are good electron donors (ref. 8). We have now determined the structures of the unsymmetrically substituted cations 6 and 7. These structures, which are shown in Figures 4 and 5, are informative both about the nature of the cyclopropenium cation and also particularly on the nature of the conjugative interactions between the substituents and the three-membered ring.



The feature that is immediately apparent on examination of the structures of 6 and 7, Fig. 4 and 5, is that in each case the three membered rings form an equilateral triangle with essentially equal C,C internuclear distances and internal angles of 60° . In each case the three atoms attached to the three-membered rings lie in the planes of these rings. The phenyl groups in both 6 and 7 are slightly twisted out of this plane so as to minimize the interactions between the two ortho hydrogens (twist angles range from 4 to 15°).

The average C,C bond distances in the three-membered rings are comparable, 1.373\AA in 6 and 1.379\AA in 7, and are very similar to those reported for 4 and 5. These average bond distances are again shorter than those of benzene despite expected bond order being substantially less than that of benzene. A curved bond path can be considered for these cyclopropenium cations which will increase the bond lengths by a significant, albeit, insufficient amount to raise the inter-nuclear distance above that of benzene. Calculations of the structure of the cyclopropenium cations support the bond distances observed here (ref. 9). Overall it is quite clear that these cyclopropenium cations can be classified on structural grounds as being fully aromatic.

There are some individual features of these structures which merit comment. In 2, the planes of the phenyl and tropylium rings are twisted with respect to each other by 29.7° . There has been considerable interest in the conformations of the related biphenyls and, apart from the parent system and one or two related biphenyls, the typical twist angle would seem to be close to 40° (ref. 5). In the case of biphenyl itself, the situation is complicated by the symmetry of the crystal and a non-equilibrium geometry is found. The C,C bond linking the two rings in 2, $1.475(13)$, would seem to be somewhat shorter than that found between the two aryl rings of biphenyls.

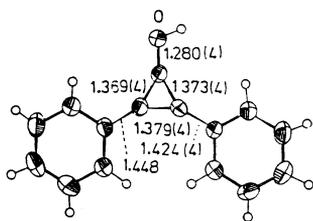


Fig. 4. Structure of 6

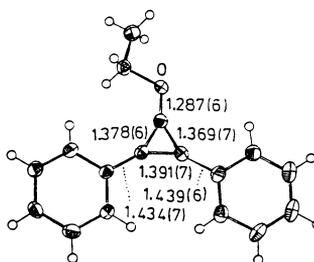
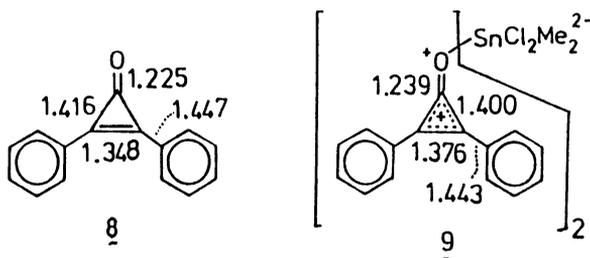


Fig. 5. Structure of 7

It is interesting to examine the changes in bond lengths on proceeding from the initial ketone 8 (ref. 10) to cations 6 and 7. As can be seen the three-membered ring in 8 exhibits considerable bond alternation and this is lost as the cations are formed. In addition there is a substantial increase in the length of the C-O bond in 6 and 7 as compared to 8, however, the C-phenyl bond distances do not change significantly. This would suggest that the degree of conjugation between the phenyl and the three-membered ring in the three compounds is not significantly different. The phenyl groups in 6 and 7 are situated such that they could conjugate effectively with the cyclopropenium rings. The degree of transfer of the positive charge onto the phenyl groups in 6 and 7 must be relatively small and indeed the downfield shift experienced in the aryl carbon resonances of 8 in its ^{13}C NMR spectrum are much smaller than are observed on protonation of diaryl ketones such as benzophenone.



The symmetrical nature of the three-membered ring in 6 and 7 means that the different substituents, OH, OCH_2CH_3 , and C_6H_5 must stabilize the positive charge to an equal extent. This is at first sight surprising as generally the two oxygen based substituents are more effective at stabilizing a carbenium ion than is phenyl (ref. 11). Bearing in mind that little charge seems to be delocalized onto the phenyl groups, then it would also seem that there is little positive charge on the oxygen atoms of 6 and 7.

Further support for the suggestion that the O atoms in 6 and 7 are not extensively involved in delocalization of the positive charge comes from the C_1OCH_2 bond angle observed in 7. This at 115.9° is less than the 120° expected for a system with a significant amount of involvement of the oxygen lone pair with the positive charge but rather falls exactly into line with the comparable angles normally found for alkyl aryl ethers. The C-O bond distances in 6 and 7 are considerably shorter than that found in 3, however, caution should be taken in a direct comparison as a result of the strained ring in these cyclopropenium cations and the resulting change in hybridization of the carbonyl carbon.

Overall, the conclusion reached from the structures of 6 and 7 is that the positive charge largely resides on the central three-membered ring. As the substituents can stabilize a positive charge in other cations, it would appear in the case of these cyclopropenium cations that the aromatic three-membered rings are sufficiently stable in their own right not to need the extra delocalization.

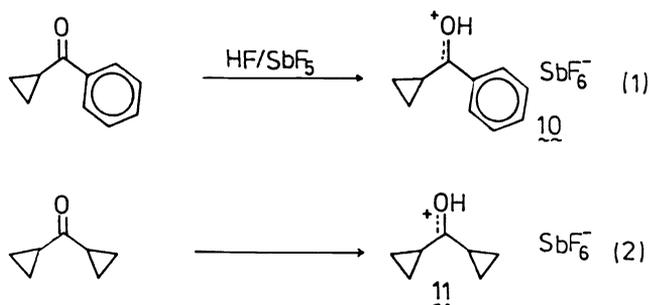
Two further points should be made. First there has been considerable discussion on the resonance energy of 8 (ref. 12). From a structural perspective there is a very marked difference in the structure of 8, which exhibits considerable bond alternation in the three-membered ring, as compared to the symmetrical arrangement in 6 and 7. The structure of 8 suggests that it is not appropriate to invoke a substantial involvement of the zwitterionic, aromatic resonance form in the ground state of this ketone. Second, complexation of the oxygen of 8 with a dialkyl tin chloride gives 9 which again does not

appear to be aromatic. This can be seen on examination of the structure of 9 (ref. 13) which is much more similar to 8 in structure than to 6 or 7. This confirms the conclusions reached on the nature of 8 and indicates something of the nature of the electron distribution in this type of Lewis acid/Lewis base complex. It is known from NMR measurements of a series of Lewis acid complexes of enones that tin based Lewis acids are far less effective in transferring positive charge onto the carbon framework of the complexed enone than some of the stronger Lewis acids such as BBr_3 or a proton (ref. 14). The conclusions reached on the basis of NMR spectral shifts are substantiated by these structural comparisons.

CYCLOPROPYLCARBINYL CATIONS

In making the transition from the aromatic cations discussed above to homoaromatic systems, it is of interest to examine the structural consequences of the interaction of a cyclopropyl ring with an adjacent carbenium ion, namely the cyclopropylcarbinylium cations. There are several theoretical investigations of the structure and bonding of these cations but no direct experimental evidence is available. The results of solvolytic studies and NMR characterization of solutions of stable cyclopropylcarbinylium cations suggest that the preferred conformation of substituted cyclopropylcarbinylium cations is one in which the three-membered ring bisects the plane of the carbenium center and that the vicinal cyclopropyl bonds are equally involved in charge delocalization. Such a suggestion is open to direct experimental test by the use of X-ray diffraction with crystalline samples of these cations.

We have prepared the two protonated cyclopropyl ketones, 10 and 11, as their hexafluoroantimonates and isolated them as crystalline solids, equations 1 and 2. The NMR spectra of solutions of these salts, which are very similar to those previously reported, are fully in accord with the indicated structures.



The structure of 10 is shown in Figure 6. There are two independent cations in the unit cell and these have identical structures within the error limits associated with the determination. It is clear from an examination of the structure of 10 that the cyclopropyl group is very close to adopting the preferred, bisected conformation. The plane formed by the three cyclopropyl carbons is at 83.4° or 87.8° from the plane associated with the carbonyl group, $C,C(O),C$, which is very close to the 90° angle required for the bisected conformation. In contrast to the cyclopropyl conformation, the phenyl group is close to being in the plane of the carbonyl group, $C,C(O),C$, (25.3° or 28.6°). The structure of 10 strikingly confirms the bisected conformation of the cyclopropylcarbinylium cation and also well illustrates the different geometries required for cyclopropyl versus phenyl conjugation with a carbenium ion.

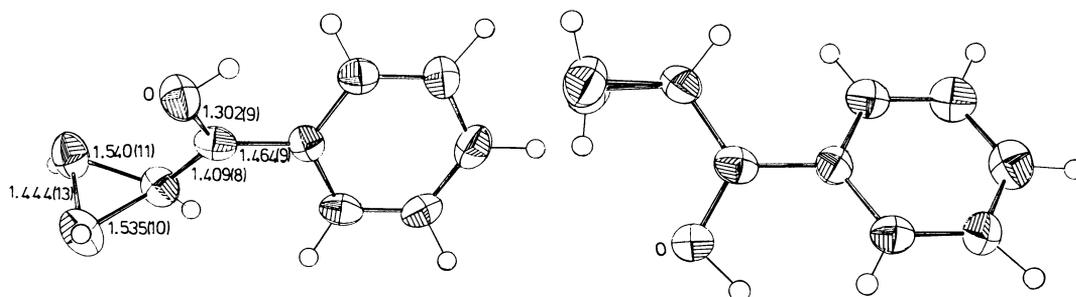


Fig. 6. Two views of the structure of 10. (Two hydrogens on cyclopropane not found.)

The bond distances observed in 10 are of considerable interest. The cyclopropyl ring is obviously very much distorted from a three-fold symmetrical structure and has two long vicinal bonds and a very short distal bond. These bond lengths in 10 can be compared with those encountered with conventional carbonyl substituted cyclopropanes. Allen (ref. 15) has carried out a detailed examination of the effect of a carbonyl substituent on the structures of a large number of cyclopropyl systems. The overall picture to emerge is that a carbonyl group causes the adjacent vicinal cyclopropyl bonds to lengthen by 0.013\AA and the distal bond contract by twice this amount, or 0.026\AA from the average cyclopropyl bond length, $1.504(3)\text{\AA}$. In the two structures of 10, the mean cyclopropyl bond distances are 1.506 and 1.514\AA , the same within experimental error of the normal distance for the neutral compounds, however, the length of the vicinal bonds has now increased by an average of 0.031\AA and those of the distal bonds contracted by an average of 0.063\AA . The changes observed with 10 are a factor of 2.4 times as large as the changes in bond distances normally encountered with carbonyl substituted cyclopropanes. The bond distance between the carbonyl carbon and the cyclopropyl carbon in 10 is shorter than that normally encountered for the comparable neutral systems, $1.409(8)$ and $1.424(9)\text{\AA}$ in 10 as compared to $1.456(6)\text{\AA}$ in the neutral compounds (ref. 15). Overall the various bond distances observed with 10 are fully in accord with the formulation of this cation as a bisected cyclopropylcarbonyl cation.

The structure found here may be compared with that calculated for the parent cation in a bisected conformation, Fig. 7, (ref. 14). The geometry shown in Fig. 7 was obtained using a 4-31G level of calculation and comparison of this with that found for 10 indicates there are some substantial differences. While the charge stabilizing effect of the hydroxy and phenyl groups will obviously attenuate the changes in bond distances observed in 10 as compared to the parent cation, it is disturbing in the calculation that the very pronounced elongation of the vicinal bonds is not matched by the contraction in the distal bond of the cyclopropane.

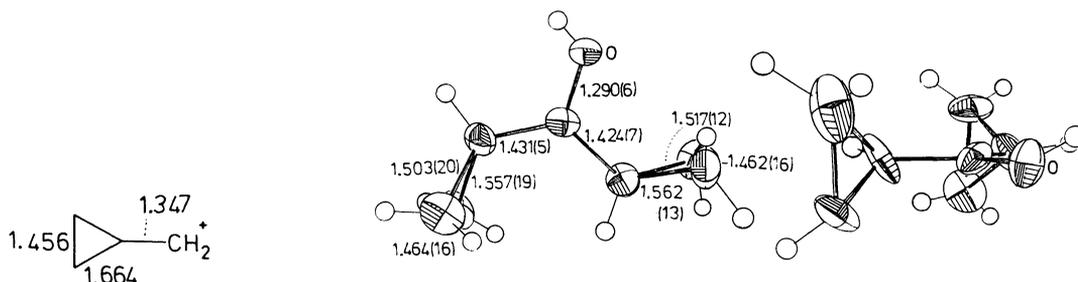


Fig. 8. Two views of the structure of 11. (one H not found.)

Fig. 7. Calculated structure of cyclopropylcarbonyl cation (ref. 14)

The structure of 11 is shown in Fig. 8. The precision of the bond distances in the cyclopropyl rings is less than that obtained for 10 but nevertheless, it is clear that the same trends are present. In the case of 11, both of the cyclopropyl rings are in a bisected conformation with respect to the central carbon of the cation with an overall sickle shape conformation.

THE STRUCTURE OF THE PROTONATED CARBONYL GROUP

Before examining the structures of some homoaromatic cations, it will be useful to explore the structure and charge distribution in the protonated carbonyl group and related alkylated derivatives. A good starting point is to consider the positions of the various anions with respect to the cations.

In the first place, in every example of a protonated carbonyl cation whose structure has been determined, an anion is always situated on or close to the plane of the carbonyl group in such a position as to accept a hydrogen bond from the proton on the oxygen atom. The interatomic distances between the carbonyl oxygens and the electronegative acceptor atoms are very short in most cases, pointing to the presence of very strong hydrogen bonds. A typical situation is shown in Figs. 9 and 10 for the case of protonated benzophenone, 12. The distance separating the carbonyl oxygen and a fluorine of an SbF_6^- is $2.639(7)\text{\AA}$ which is less than the sum of the Van der Waal radii for O and F (2.8\AA).

In addition to this in-plane hydrogen bonding interaction, in nearly every case examined two additional counterions are found close to the protonated carbonyl group. These are arranged approximately 3\AA above and below the plane of the carbonyl and are located on or very close to the plane which lies on the axis of and at 90° to the plane of the carbonyl group itself.

This is illustrated with 12 in Fig. 10. In this case the closest fluorines in the two anions form acute angles ($F-C-O = 76.2^\circ$ and 75.7°) with respect to the protonated carbonyl group. Not all of the structures we have determined have such an acute angle between counterion and the carbonyl and there seems to be variation in this angle. However, in only one or two cases does the angle ever exceed 90° and in no case does the angle reach 110° . With the proviso that at present all the distances between the carbonyl carbon and the electronegative atom above and below the plane of the protonated carbonyl is at least 2.8\AA , it would seem that the 110° angle found in the approach of a nucleophile to a neutral carbonyl compound is not adhered to in the case of the protonated carbonyl. This finding could have quite considerable consequence in the extension of the Baldwin rules of stereo-electronic control to acid catalysed reactions of carbonyl compounds (ref. 17).

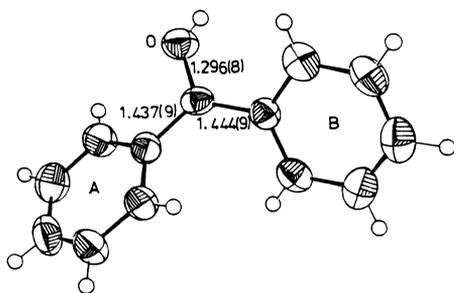
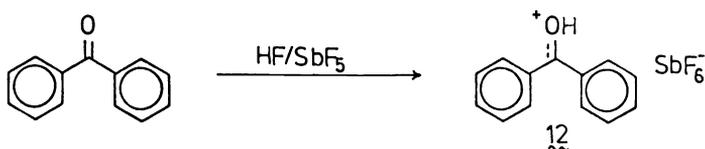


Fig. 9. The structure of 10. Twist of phenyls to $C-C(O)-C$ plane, A 28.0° , B 31.8° .

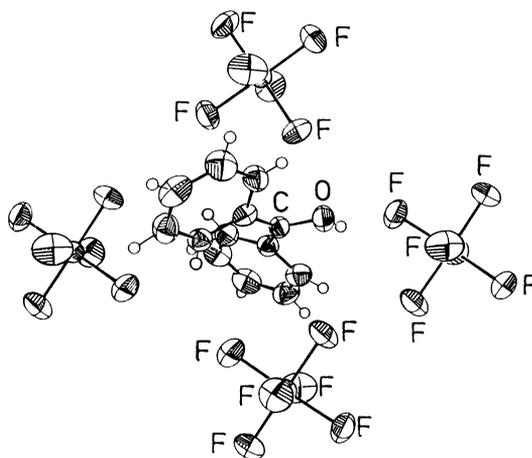


Fig. 10. The relationship of SbF_6^- counterions to 10.

In order to see any systematic variation in bond distances as a function of charge stabilizing ability of the groups attached to a protonated carbonyl group, we have started to prepare a series of protonated benzophenones with different substituents in the para positions. Protonated di-*p*-methoxybenzophenone fluorosulfate, 13, was prepared and its structure determined. In this case two independent cations were present in the unit cell, both of which had very similar structures, one of which is shown in Fig. 11.

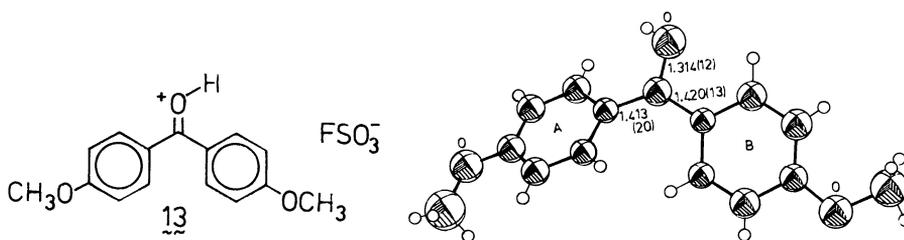


Fig. 11. The structure of 13. Twist of phenyls from $C-C(O)-C$ plane, A 30° ; B 24°

In order to obtain a cation with different substituents on the two phenyl rings we attempted to prepare protonated *p*-chlorobenzophenone hexafluoroantimonate using the same procedure as was successful in the case of 12. On determining the structure it became apparent that instead of a 'simple' cation, a dimeric system was present in which the proton on the carbonyl oxygen of one species was hydrogen bonded to the oxygen of another benzophenone, Fig. 12. The O-O distance in this dimeric situation is exceptionally short (2.468Å) and well below the sum of the van der Waals radii of these atoms. At first glance this structure is unusual but, bearing in mind the necessity of having a good hydrogen bond acceptor to interact with the carbonyl proton, this dimeric situation represents a further type of example of the general pattern found in these protonated carbonyl structures. (A further example of this dimeric type of structure will be presented later.) While this dimeric structure is found in the crystalline state, it is very likely that similar species are found in solution when acid catalysed reactions of carbonyl compounds are carried out in hydrocarbon or related solvents.

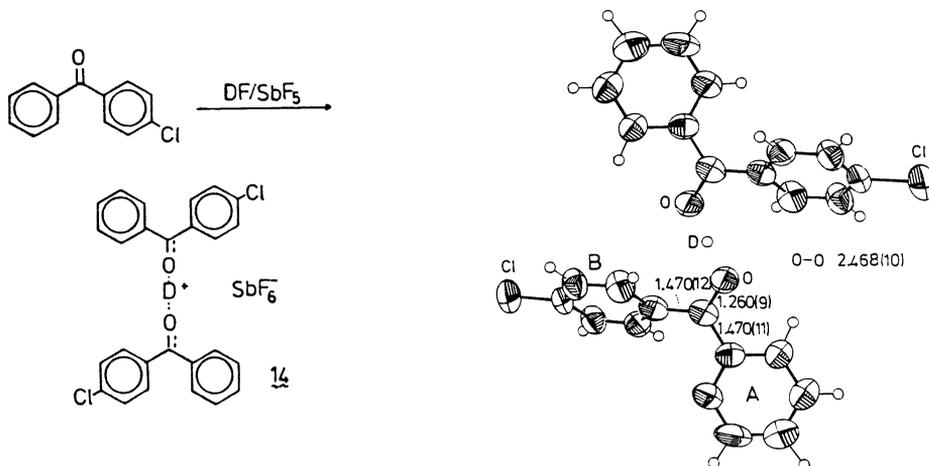


Fig. 12. Structure of 14.
Twist of phenyls from C-C(O)-C plane, A 17.9°; B 43.3°

In passing it is interesting to note in the structure of 14 that the phenyl ring bearing the chlorine is twisted out of conjugation with the π system of the carbonyl group, while the other unsubstituted phenyl is closer to the plane of the carbonyl group. This would seem to be consistent with the known donor properties of the two rings although more structure determinations are needed before it can be seen whether this will be a general phenomenon with unsymmetrical benzophenones.

In discussing trends within this series of cations the first thought is to discount 14 from the series in as much as at most only half of the positive charge can be located on either of the two organic fragments. However, in view of the very strong hydrogen bonding interaction found in all of the cations, it is unlikely that a full positive charge is induced on any of the organic fragments in these systems.

There is a systematic change in bond distances in these protonated benzophenones. As the stability of the cation increases, 14 being the least and 13 the most stable, there is an increase in the C-O bond distance. This change in the C-O distance is accompanied by a corresponding change in the C-phenyl bond distance. This is shown clearly in Fig. 13 in which these bond distances are plotted against each other. The linear correlation observed with the three cations can be extended to include neutral benzophenone. It is quite clear from this correlation which extends over a very considerable range of bond distances, that the changes in structure of these cations are quite systematic. The changes seem to be related to the stability of the cations and reflect the amount of charge which resides on the carbon framework.

The C-O bond distances observed with the protonated carbonyl cations are intermediate between the length of a typical carbonyl bond, 1.22Å and a C-O single bond, 1.37Å. This means that the bond order of the C-O bond in these protonated systems is intermediate between that of the C=O double and single bonds. Conventionally, this would be depicted in terms of the two first two resonance structures shown in equation 3. However, there is an additional resonance structure which must be considered in which the charge is located on the OH proton. The question arises as to what is the relative importance of these three structures and how the proportion changes as the cation becomes less stable and the C-O bond distance is shortened.

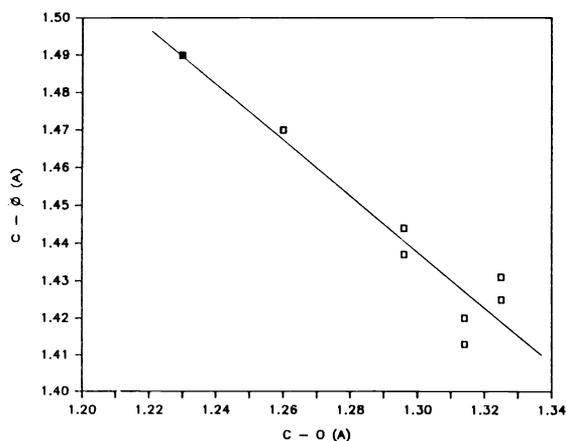
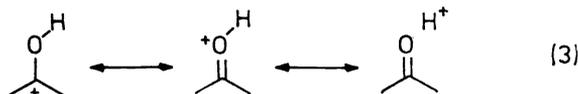


Fig. 13. Correlation between C-O and C-phenyl bond distances in neutral and protonated benzophenones.

It has already been shown that there is a very strong hydrogen bond between the OH proton and an electronegative atom in these protonated carbonyls.

Theoretical studies of the structure and charge distribution in this group suggests that the OH proton is acidic and that a considerable fraction of the total positive charge is located on this proton. In other words the third resonance structure shown in equation 3 can not be neglected. Indeed it is interesting to note that there appears to be a correlation of the O-O distance between the carbonyl oxygen and oxygen of the anion in 13 and 14, with the shortest distance being observed in 14 where the C-O distance is also the shortest. This would suggest that as the bond order of the C-O bond increases that there is a corresponding decrease in the bond order of the O-H bond although more structures are needed before this point can be confirmed.

In order to further probe the distribution of positive charge in these cations it is informative to derive some bond orders corresponding to the distances observed with these cations and in particular to examine the sum of bond orders for all the bonds to a particular atom. In order to determine the relative contribution of the various resonance structures shown in equation 3 it is helpful to focus attention on the valence of the oxygen atom of the carbonyl. The importance of the second resonance structure should be apparent in a bond order sum for the carbonyl oxygen.



In order to use this approach, it is important to know the bond distances about the oxygen atom reasonably precisely and also to ensure that there are no other contacts within the crystal lattice which will contribute. This creates a difficulty with the protonated carbonyls in as much as the OH proton is not well defined in terms of its position. Instead, this approach will be used with some O-substituted derivatives of these cations. The C-O bond distances of the carbonyl bond in these O-alkyl substituted cations have very similar distances to the corresponding protonated carbonyls and they thus provide good models for the charge distribution in the latter systems.

Excluding the cyclopropenium cations from discussion as there are concerns with a possible distortion of the bond distances due to the constraints of the three membered rings, the one such O-substituted system discussed so far is that of 3. In this cation the C-O bond distances are 1.356Å which correspond to a bond order of 1.05 (ref. 18). This gives a bond valence sum for the oxygen of 2.10 suggesting that the lone pairs on the central oxygen are not significantly involved in charge delocalization. Such a picture is quite consistent with the lack of any bond alternation in the seven-membered rings of 3.

We have determined the structures of several simpler ethoxy substituted carbenium ions and find a very similar pattern of bond distances in each of these. Only one case will be presented here, namely 15, which has been selected as it is particularly informative on the question of charge distribution. The structure of this cation which was prepared as its hexachloroantimonate by treatment of the corresponding lactone with Meerwein's reagent is given in Fig. 14.

As can be seen from the structure, five of the six atoms forming the lactone ring in 15 lie essentially on a single plane with only the sixth carbon atom being significantly removed from this plane. The ethoxy group also lies in this plane and adopts the conformation expected on stereoelectronic grounds. Of particular interest are the various C-O bond distances in this structure. First, it will be noted that the two C-O partial double bonds

still have approximately the same length (1.282 and 1.254Å) as is found for the protonated carbonyl compounds. However, the two formal C-O single bonds are now exceptionally long, and indeed the O-C₉ bond at 1.534Å is the longest known C-O bond distance! The lengthening of the C-O single bond in the ethoxy group would seem to be coupled with a shortening of the C-O 'double' bond distance. Converting these bond distances to bond orders and summing them for the two oxygens in 15 gives values of 2.08 (ring oxygen) and 2.02 for the ethoxy oxygen. These values have considerable errors attached with them, however, it would seem clear that the two oxygen atoms in 15 are both better represented as being divalent rather than trivalent.

This means that in these protonated and alkylated carbonyl cations that double bonding between the carbon of the carbonyl and the oxygen atom occurs at the expense of a reduction in the bond order of the group, H or ethyl in this latter case, attached to the oxygen. In other words, as the carbonyl bond is shortened, positive charge is transferred onto the group attached to the oxygen atom. This is apparent in the structure of 15 in which the O-C₉ bond is the longest, as would be expected as positive charge would be the most stable on this tertiary carbon. There is also a contraction of the CH₃-CH₂ bond distance (1.456Å) from the value normally associated with ethyl esters (1.503Å) (ref. 19). Such a shortening is quite consistent with the presence of charge on the CH₂ carbon.

The analysis presented above essentially means that of the three resonance structures shown in equation 3, it is the first and third which are the most important in describing the charge distribution in the protonated and alkylated carbonyls. While this is not the way the organic chemist conventionally writes the structure of the protonated carbonyl, such a formulation is quite consistent with the electronegativities of the various atoms.

HOMOAROMATIC CATIONS

To this point we have examined the structures of a series of cyclic cations containing $4n+2$ π electrons and shown that their structures are fully in accord with them being designated as aromatic. The cyclopropylcarbiny cation was also examined and it was shown that the interaction of a cyclopropane with a positively charged center has some pronounced geometric consequences on the structure of the three-membered ring.

One way of constructing a homoaromatic system is to replace a double bond in an aromatic system by a cyclopropane and allow this group to interact with the remaining unsaturated system. From the information presented so far, it is clear that if the inserted cyclopropane is involved in electron delocalization then this should be apparent in the structure of the cation and it is this topic which is explored in the following sections of this paper.

Homotropylium cations can be considered to be derived from a tropylium cation in which one of the double bonds has been replaced with a cyclopropane. The conventionally accepted picture of the delocalization in such a cation can be summarized in terms of the resonance structures shown in equation 4. As such, the internal cyclopropane bond distance would be expected to be considerably longer than either of the two external bonds and the structure would be expected to be quite different from that of the cyclopropylcarbiny cations.

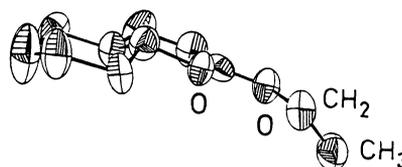
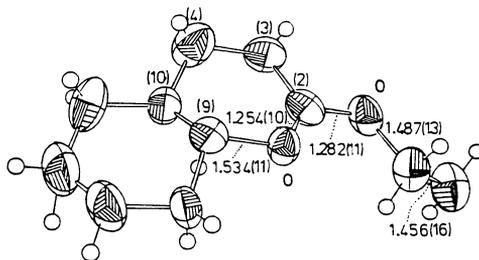
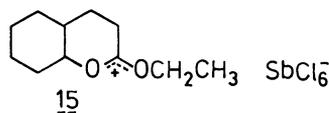
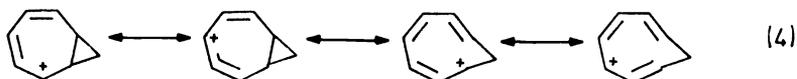
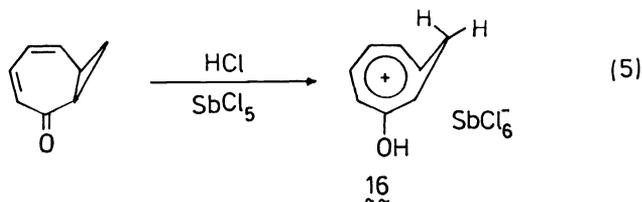


Fig. 14. The structure of 15.

Our first foray into the structure determination of homotropylium cations involved the 2-hydroxyhomotropylium cation, 16, (ref. 20). This cation exhibits the typical ^1H NMR spectrum of a homotropylium ion with a large chemical shift difference between the two methylene proton resonances. In the case of 16 this difference is 3.10 ppm which, as would be expected with the charge stabilizing hydroxy group at C_2 , is somewhat smaller than the 5.86 ppm difference observed in the case of the parent cation. The ^{13}C NMR spectrum of 16 was found to be essentially the same in solution as well as in the solid state indicating that there is no major change in conformation or electron distribution in the two phases.



The structure of 16 is shown in Fig. 15. Unfortunately, the cation is disordered in the crystal with a pseudo-mirror plane running through C_8 , the mid point of the C_1, C_7 bond, and C_4 . This means that it is not possible to differentiate the position of the hydroxy group from being located on C_2 or C_6 . Despite this disorder, the bond distances about the cyclopropane ring are well defined and clearly show a totally different pattern of bond distances to those encountered above for a cyclopropyl carbanyl cation. The internal bond of the cyclopropane (1.626(8)Å) is much longer and the external bonds (1.488(7)Å) shorter than would be expected for a regular cyclopropane. The relatively short C_1, C_2 (C_6, C_7) bonds also support the suggestion of the involvement of the internal cyclopropane in charge delocalization. The structure of 16 is quite consistent with a homoaromatic formulation of this cation.

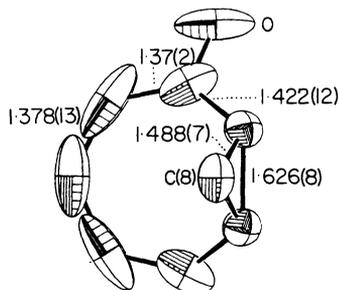


Fig. 15. The structure of 16.

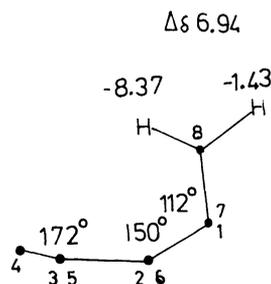
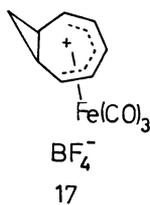
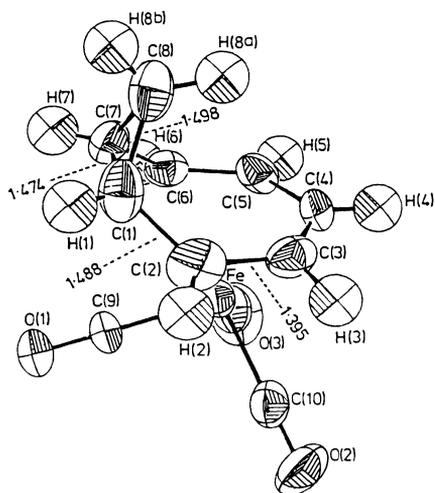


Fig. 16. Conformation of 16 and calculated chemical shift differences of C_8 protons in parent cation.

The overall conformation of 16 is very similar to that calculated by Haddon for the parent homotropylium cation (ref. 21). Assuming the same conformation for the parent cation, it has been possible to calculate the difference in chemical shifts that would be expected for the resonances of the C_8 protons (ref. 22). These calculations take into account the contributions due to the presence of an induced ring current and also local magnetic anisotropic effects. The interesting feature to emerge from these calculations is that both of the C_8 protons are shielded, Fig. 16. This is a surprising result in view of the generally accepted dogma of proponents of homoaromaticity that the origin of the large chemical shift differences of these methylene protons is due to the endo proton being shielded and the exo deshielded as a result of an induced ring current. The overall chemical shift difference between the two methylene protons can still be accounted for on the basis of these calculations, but there are substantial difficulties in accommodating the expected intrinsic chemical shift of these protons in the absence of a ring current effect. This observation throws into question the use of the chemical shift difference of the bridging methylene protons in a homotropylium cation as a criterion of homoaromaticity, a point we will return to later.

Further information on the structure of the 2-hydroxyhomotropylium cation can be gained from an examination of the non-homoaromatic iron complex, 17. This cation, which exhibits a very small chemical shift difference between the C₈ exo and endo protons, was one of the original cornerstones in the argument for the homoaromatic nature of the homotropylium cations (ref. 23). The iron complex 17 was isolated as its tetrafluoroborate and its structure



determined using X-ray crystallography, Fig. 17. The short internal cyclopropane bond observed in 17 confirms the original formulation of this cation and gives overall support to the conclusions reached concerning the structure of 16.

In addition to this structural approach to the definition of the type of electron delocalization in 16, we have also measured the heats of protonation of a series of unsaturated ketones, including 2-homotropone (ref. 24). The results of this study give good thermochemical evidence for the homoaromatic formulation of 16.

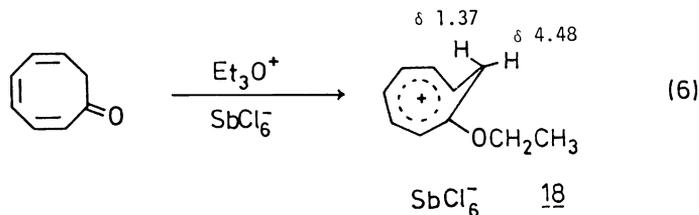
Fig. 17. The Structure of 17

A SECOND HOMOTROPYLIUM CATION CONFORMATION

Haddon, in his theoretical exploration of the homotropylium potential energy surface, suggested that there were two energy minima (ref. 21). The lowest energy of these corresponded quite closely in structure to that found here for 16. The second energy minimum, which occurs along the pathway for the ring inversion process of the homotropylium cation and was calculated to be some 6–10 kcal/mol less stable than the former conformation, was distinguished by a very long C1–C7 bond distance of 2.303 Å (MINDO-3).

The relative energies of these two quite different conformations of the homotropylium cation should depend on the position and nature of any substituents. Electron donor groups at C₁, C₃, C₅, and C₇ should favor the cyclooctatrienylium resonance structures as positive charge is maximized at these carbons in the open form of the cation. Conversely, donor substituents at C₂, C₄, and C₆ would be most effective in stabilizing the cation when it is in the closed bicyclo[5.1.0]octadienyl form. In view of the relatively small energy difference between the two conformations, it should in principle be possible to invert their relative energies by the appropriate placement of substituents. This is indeed the case as we have now shown with the 1-ethoxyhomotropylium cation.

Cation 18 was prepared as its hexachloroantimonate, equation 6. The ¹H NMR spectrum of this salt exhibits a large chemical shift difference between the C₈ methylene protons (3.12 ppm) that is typical of homoaromatic cations and indeed is directly comparable in magnitude to that to 16. The ¹H NMR spectrum of 18 is very similar to the previously reported 1-hydroxy and 1-methoxyhomotropylium cations. The ¹³C NMR spectra of 18 were very similar in solution and solid phases indicating once more no significant change in the conformation or electronic structure of the cation in either phase.



The structure of 18 is shown in Fig. 18. It is immediately obvious on examination of this structure that there is a very long inter-nuclear distance between C_1 and C_7 (2.284(5) Å). This distance, and indeed the overall conformation of the cation corresponds closely to the structure calculated by Haddon for the second energy minimum on the homotropylium energy surface. This agreement is remarkable and attests to the power of the theoretical approach to predicting the conformation of even these relatively large cations.

With a more detailed examination of the structure of 18, it is clear that there is a progressive increase in the degree of bond alternation on proceeding from C_1 around the unsaturated portion of the ring. In fact, the C_6-C_7 bond distance (1.336(6) Å) is the same as that normally encountered with a double bond in a polyene, e.g. cyclohexadiene, 1.339 Å, hexatriene, 1.343 and 1.329 Å, suggesting that this bond is not significantly involved in the delocalization of the positive charge in the system. In this regard it is interesting to examine the various torsional angles between adjacent C-C bonds around the 7-basal carbons of 18. Apart from one exception, these torsional angles are relatively small and should not interfere with π -delocalization. The exception is the $C_{4,5}-C_{6,7}$ torsion angle for which a value of 37° is found. This approaches the 45-55° torsion angle limit to effective π -delocalization which has been found in the bridged annulenes. This relatively large value of the $C_{4,5}-C_{6,7}$ torsion angle reinforces the suggestion that the C_6, C_7 double bond is not extensively involved in the delocalization of the positive charge.

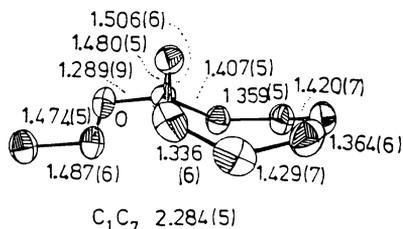


Fig. 18. The structure of 18

The C_1, C_8, C_7 bond angle in 18 is 101.1(6)°. This is smaller than the tetrahedral angle suggesting perhaps that there is a bonding interaction between C_1 and C_7 . If this were the case then C_1 and C_7 should both be distorted from a trigonal geometry. This is not so. For example, C_1 lies exactly in the plane defined by C_8, C_2 , and O. The same would seem to be the case for C_7 although the position of H_7 is not so well defined. The 101° bond angle at C_8 and the planarity of the 'bridging' carbons C_1 and C_7 mean that any interaction between these two carbons formally involves two p orbitals intersecting at an angle of 80.3 to each other, 1.77 Å from each carbon. With this spatial arrangement of C_1 and C_7 , any interaction between these two carbons must be very weak. It has to be concluded on structural grounds that there is little evidence to support 18 being designated as homoaromatic.

To further define the nature of 18 the heats of protonation of a series of related ketones, including the eight membered ring compounds 19, 20, and 21, have been determined, Fig. 19.

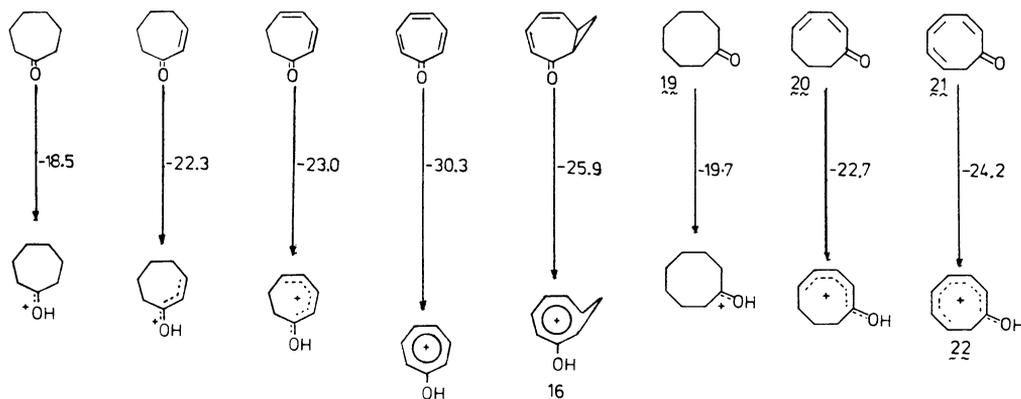


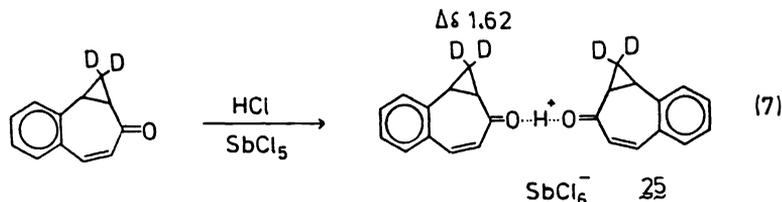
Fig. 19. The heats of transfer ΔH_{tr} of various ketones into FSO_3H at 25°C.

The differences in the heats of transfer into FSO_3H (ΔH_{tr}) of the seven-membered ring ketones has been discussed previously in terms of the homoaromatic stabilization of 16. The marked increase in ΔH_{tr} on proceeding from the cycloheptadienone to 2-homotropone (2.9 kcal/mol) was taken to be good evidence for the "extra" stability of 16 resulting from the cyclic delocalization in this cation. The changes in the heats of transfer, ΔH_{tr} of the eight-membered ring ketones stand in marked contrast to the results obtained with the seven-membered series. In this series we have as yet been unable to obtain reproducible data for the protonation of cyclooctenone, however, the differences in ΔH_{tr} of 19 and 20 into FSO_3H is of the same order of magnitude as was found from the seven-membered ring ketones. Addition of the third double bond to the eight-membered ring, ie 20 \rightarrow 21, does not in this case produce a substantial increase in ΔH_{tr} but rather the magnitude of the heat of

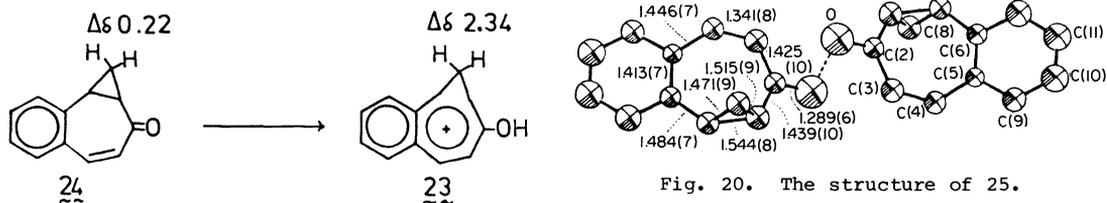
transfer is not much out of line with what would be expected for a linear polyenone. We have previously shown (ref. 24) that the 1-hydroxyhomotropylium cations are thermodynamically less stable than the isomeric 2-hydroxyhomotropylium cations; a result which is quite consistent with these heats of protonation. It must be concluded that there is no thermochemical evidence to support a homoaromatic formulation of the structure of 22.

The conclusion that 18 is not homoaromatic that comes from the analysis of the structure and thermochemistry of this system, would seem to be at odds with the ^1H NMR evidence, and particularly the large chemical shift difference between the two methylene proton resonances. However, this is not a unique situation. Cycloheptatrienes exhibit a directly comparable geometry about the analogous potential homoconjugate bond between C_1 and C_6 as has been found here for 18. The bond distances in the seven-membered rings of cycloheptatrienes are typical of a simple unsaturated system and there is no compelling structural evidence to suggest that they be regarded as homobenzenes. On the other hand, the diamagnetic susceptibility exaltations of cycloheptatrienes, which are a measure of the magnitude of an induced ring current, are very large and can in several instances exceed that of benzene (ref. 25). Thus cycloheptatrienes exhibit an induced diamagnetic ring current when placed in a magnetic field, however, cycloheptatrienes are not normally considered to be homoaromatic. It would seem that the presence of an induced diamagnetic ring current is a poor indicator that a molecule or ion is homoaromatic.

The structure of a further homotropylium cation has been determined in our laboratories. In this case the situation is somewhat more complex in as much as further example of a dimeric species was isolated, equation 7. (The presence of the deuteriums in this cation reflect material availability rather than some other ulterior motive.)



The intent of the original preparation was to isolate 23 and to determine its structure in order to provide a further example of a 2-hydroxyhomotropylium cation. Dissolution of 24 in FSO_3H gives 23 which exhibits the characteristic chemical shift difference between the two methylene protons (ref. 26). The presence of the benzene ring would seem to attenuate the magnitude of this difference as compared to 16 as would be expected, however, in comparison with the shifts of 24 it would again seem clear that there is evidence for an induced diamagnetic ring current.



The chemical shifts of 25 when dissolved in CH_2Cl_2 are intermediate between those of 23 and 24. Typically the shifts experienced by the various protons in the conversion of 24 to 25 are some 70% as large as those found on going from 24 to 23. However, the pattern of shifts observed with 25 is the same as those of 23 suggesting that the two seven-membered rings in the dimer are homoaromatic but that there is a somewhat attenuated degree of charge transfer onto the organic framework. A similar linear relationship of chemical shifts as a function of systematic substituent changes in an oxygen substituted homotropylium cation has been noted previously (ref. 20).

The structure of 25 is shown in Figure 20. The overall conformation of the seven-membered ring is once more very similar to that seen for 16 and 18, and a similar pattern of bond distances would be expected to those found for 16. However, the structure is once more inconsistent with a homoaromatic formulation of this dimeric cation. The telling feature in this cation is the unsaturated portion for which the bond lengths found are typical of a neutral system. In other words there does not appear to be any substantial involvement of the double bond or phenyl group in the delocalization of the positive charge. In terms of the cyclopropane there are some significant structural changes. While the internal cyclopropane bond in 25 is relatively long (1.544(8) Å), there is a contraction of the $\text{C}_7\text{-C}_8$ bond (1.471(9) Å). These cyclopropane bond distances, coupled with the relatively short $\text{C}_1\text{-C}_2$ bond (1.439(10) Å), are just what would be expected for a cyclopropyl carbonyl cation with a phenyl substituent. From a structural perspective this dimeric cation is best described in terms of a cyclopropylcarbonyl rather than a homoaromatic type of delocalization.

Once more this conclusion is at odds with the NMR result and points to the caution that must be placed on the use of NMR as the sole criterion of homoaromaticity in these homotropylium ions. We would repeat the suggestion made earlier that where the sole evidence for homoaromaticity is the ^1H NMR spectrum, or related susceptibility measurements, then it is more appropriate to use the term diatropic rather than homoaromatic and reserve the latter classification for molecules or ions where there is additional more reliable information available such as structural or thermochemical results (ref. 25).

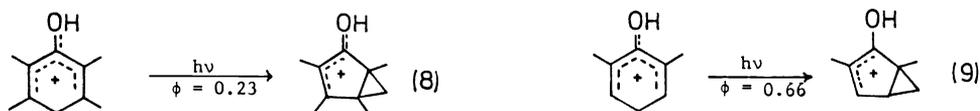
THE ANTI-HOMOAROMATIC BICYCLO[3.1.0]HEXENYL CATIONS

Formally, the bicyclo[3.1.0]hexenyl cations can be considered to be derived from the non-aromatic cyclopentadienyl cations. They represent an interesting situation in which a cyclopropyl ring is positioned across the ends of an allyl cation and as such involvement of the internal cyclopropane bond would formally lead to an antihomoaromatic cation. The structural consequences of such a situation are particularly intriguing.

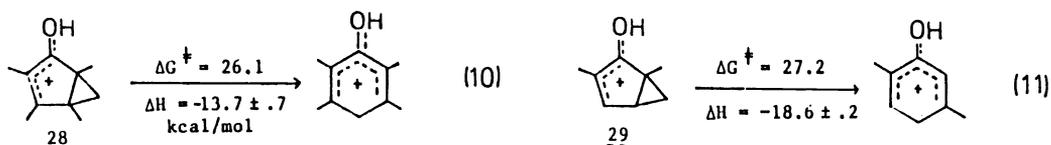
There are a substantial number of reports on the preparation and reactions of the bicyclo-3.1.0]hexenyl cations and it is generally agreed that they are not aromatic (ref. 27). In particular, the NMR spectra of these cations shows no evidence for the presence of an induced ring current and also, and most importantly, the breaking of the internal cyclopropane bond to give the isomeric cyclohexadienyl cations involves a substantial energy barrier. In terms of electron delocalization in these cations, it is has been suggested that the external, rather than the internal cyclopropane bonds are involved in charge delocalization. If this is the case then in terms of the structure of these cations the internal cyclopropane bond would be expected to have a normal, or perhaps even shorter than normal bond distance, whereas the two external bonds would be lengthened. Such a structure is not that which would be expected in the absence of any special effect due to the number of electrons in the cyclic system and the determination of the structure of a bicyclo[3.1.0]hexenyl cation would be a good test of the importance of homoaromaticity.

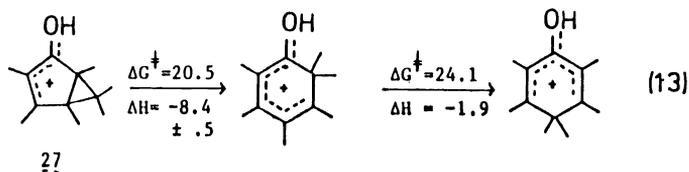
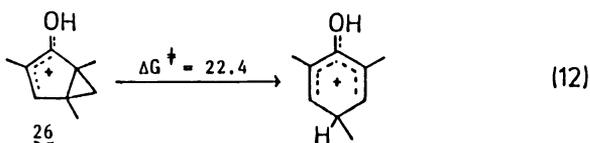
A major difficulty in the isolation of a bicyclo[3.1.0]hexenyl cation as a crystalline solid comes from the thermal stability of these bicyclic systems. While the barriers to the thermal isomerization of these cations to the isomeric cyclohexadienyl cations are relatively high, these reactions still usually take place at below room temperature. Such a facile isomerization places formidable technical difficulties in the physical handling of these cations and instead of embarking on such a course of action, we have sought simple examples of these cations in which the barriers to isomerization are sufficiently high to allow manipulation at ambient temperatures for short periods of time.

From the results of a project in the use of carbocations in the storage of solar energy (ref. 28), we have examined the photochemical reactions of a series of protonated phenols and shown that it is possible to prepare a wide range of bicyclo[3.1.0]hexenones by irradiation of these cations in strong acid solutions. The interesting feature of these reactions from the perspective of this work is that with the use of triflic acid as a strongly acidic, but weakly oxidizing solvent, these photochemical reactions can be carried out at room temperature. The protonated bicyclo[3.1.0]hexenones are thermally stable under these conditions, equations 8 and 9.



All of the protonated bicyclo[3.1.0]hexenones we have studied eventually isomerize on heating in triflic acid to yield the corresponding protonated phenol. This thermal isomerization is of interest in its own right as it throws considerable light on the nature of the electron distribution in the cations. By monitoring the course of the reactions by NMR spectroscopy, the rate constants and activation parameters of these isomerizations could be determined. As the isomerizations were also very clean with no side products or decomposition being detected, it was possible to measure the heat released during this isomerization using differential scanning calorimetry. Some representative results are summarized in equations 10 - 13.





As under the conditions used the phenols do not undergo any further isomerizations involving migration of the methyl groups around the ring, it is clear that the ring opening of the cyclopropane of these bicyclic cations is not straightforward and at least three different reaction paths must be operative. Only in the case of 26 does the internal cyclopropane bond appear to open with out any scrambling of the positions of the ring carbons. In the other examples shown, the C₆ carbon either ends up as C₄ or C₆ of the resulting phenol. These latter reactions are reminiscent of the findings of Hart with 27, in which it was shown that the three-membered ring moved around the five-membered ring more rapidly than opening to the protonated cyclohexadienone. It would seem from these results that comparable reactions could occur in the ring opening reactions of 28 and 29, even though the cyclopropanes do not have any substituents at C₆. The nature of these ring openings can be accounted for in terms of the substituents on the rings.

The second and startling point to emerge is the magnitude of the energy changes associated with these isomerizations. Thus for the isomerization of 29 to 30, despite the overall reaction being exothermic by 18 kcal/mol, there is a large free energy of activation associated with the reaction. (As the entropy changes associated with these isomerizations would appear to be small and it is possible to use ΔG^\ddagger as a reasonable approximation for ΔH^\ddagger .) This is an exceptionally large activation barrier for a carbenium reaction which is so exothermic. It is not clear at this stage whether the circumambulatory or ring opening step is rate determining in the isomerization of 29 to 30, however, it is clear that the direct ring opening of 29, the reaction corresponding to a homoaromatic type of delocalization of the cyclopropane, must have an even higher activation energy. In short, no evidence would be expected in the structures of these cations for delocalization of the internal cyclopropane bond.

STRUCTURAL STUDIES

To this point we have been able to prepare only one example of a crystalline bicyclo[3.1.0]-hexenyl cation, namely cation 28 as its SbCl₆⁻ salt. During the structure determination it became clear that a molecule of water had been incorporated into the crystal lattice at some stage during the manipulations, however, the presence of the water does not affect the structure of the cation, Fig. 21.

The water incorporated into the crystal of 28 is located in the plane of the protonated carbonyl group hydrogen bonded to the OH proton. The question arises with this structure as to whether the proton is on the water yielding a hydroxonium ion with the carbonyl group hydrogen bonded to this, or whether the proton is bonded to the carbonyl oxygen and hydrogen bonded to the oxygen of the water. The latter situation would be expected on the relative basicities of water and the ketone corresponding to 28 (ref. 29). That this is the case with 28 is readily apparent on examination of the its structure, Fig. 21, where for example, the C-O bond distance of the carbonyl group (1.279(7)Å) is the same as that normally found for a protonated carbonyl.

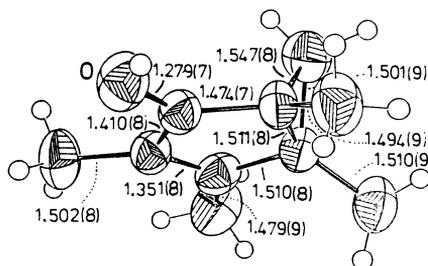


Fig. 21. The structure of 28.

It is obvious on examination of the structure of 28 that it by no means corresponds to a normal protonated cyclopropylketone. The bond distance around the cyclopropane are quite different from those found above for 10 and 11 or any of the homotropylium cations discussed in the previous section. It could be argued that one would not expect the structure to correspond to that found for 10 and 11 in as much as there are in reality electron acceptor substituents on two different carbons of the cyclopropane. Allen has examined the effect of two electron accepting substituents on a cyclopropane and has shown that the common bond between the two substituents is longer and the other two bonds shorter than a normal cyclopropane bond distance (ref. 15). This is not the case with 28 where the internal cyclopropane bond is no longer than that normally encountered for a cyclopropane. In fact it is one of the external cyclopropane bonds in 28 which would appear to be significantly lengthened. This finding is consistent with the conclusions based upon NMR results of charge delocalization into the external cyclopropane bonds. The way the cyclopropane in 27 becomes involved in charge delocalization is clearly quite different from a normal cyclopropyl carbanyl situation and also quite different from that encountered in the homotropylium cations.

In comparing the structure of 28 with that of the cyclopropyl ketones discussed above there is one further point of difference. This comes in the length of the bond from the carbonyl carbon to the cyclopropane. In the structures of 10 and 11, the mean length for this bond is 1.422(9)Å (four structures). This is considerably shorter than that found here for the comparable bond, 1.474(7)Å. It is also of significance that the bond distance between C₄ and the cyclopropane (1.510(8)Å) is also longer than would have been expected. Charged models are not available for comparison in this case, but this distance would even seem long in comparison with neutral systems in which a sp² carbon is bonded to a cyclopropane (ref. 15). Why are these two bonds in 28 significantly longer than would be expected on the basis of model compounds? We would suggest that the lengthening of these bond is one way in which the cation can lessen the effect of the interaction of the internal bond of the cyclopropane with the allyl moiety in 28. In other words, 28 would seem to be showing evidence of antihomoaromaticity and undergoing a bond lengthening which is directly comparable to the distortion of cyclobutadiene from a square to a rectangular structure. Clearly we need to examine a wider range of these cations but we would suggest that the structure of 28 is quite consistent with this cation being designated as antihomoaromatic rather than simply non-aromatic.

CONCLUSION

It is clear from the results that we have presented in this paper that the determination of the structures of carbenium represents a rich new area of investigation. The results obtained are not always predictable and in many instances seem to contradict the current thinking of the structure and charge distribution of these cations. In presenting these results and conclusions we are very mindful of the need for caution in the overall interpretation of crystallographic data and particularly the need to examine a much wider range of examples, however, it is quite clear that the subject of homoaromaticity is not dead and that there remains much to be done before these systems are fully defined.

ACKNOWLEDGEMENT

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