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Small-ring carbenes carrying a positive charge: the effects of substituting by CN in c-$C_4H_3^+$

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Abstract

Calculations at B3LYP/6-31+G(d) show c-$C_4H_3^+$ to have a singlet ground state, with the triplet being 19.5 kcal mol^{-1} higher in energy. Singlet c-$C_4H_3^+$ has a puckered ring structure (C_s symmetry) with an out-of-plane angle of 51.4°. The barrier to inversion via the planar ring structure (C_{2v} symmetry) is 29.1 kcal mol^{-1}. In the puckered ring the cross–ring distance between CH groups is 1.793 Å and the Wiberg bond order is 0.436, indicating considerable interaction. The stability of the singlet state then is attributed to homoaromaticity. Ion c-$C_4H_3^+$ in its triplet state is planar, but with alternate bonds being long and short, reminiscent of the geometries of c-C_4H_4 and c-$C_4H_4^+$. Substitution of H atoms by CN groups stabilises the triplet state relative to the singlet, and for $C_4(CN)_3^+$ the triplet is only 8.4 kcal mol^{-1} higher. Substitution also reduces the out-of-plane angle of the ions in the singlet state, going from 51.4° in the unsubstituted ion c-$C_4H_3^+$ to 43.4 kcal mol^{-1} in $C_4(CN)_3^+$. A CN group adjacent (α) to the carbene centre reduces the barrier by ~7 kcal mol^{-1} whereas substitution at the opposite carbon (β position) reduces it by ~2 kcal mol^{-1}. These effects are roughly additive, with $C_4(CN)_3^+$ having a barrier to inversion of only 12.9 kcal mol^{-1}. (Int J Mass Spectrom 195/196 (2000) 393–399) © 2000 Elsevier Science B.V.

Keywords: Derivatised C_4 cations; CN substituents; Homoaromaticity; Singlet/triplet splitting

1. Introduction

Recently we have discovered that cyanoacetylene reacts with C_{60}^{2+} in the gas phase to produce $C_{60}^{+\cdot}$ and a dimer radical cation $C_6N_2H_2^{+\cdot}$ [1]. The latter cation is very stable toward collision-induced dissociation and, at high energies, loses either a CN group or a hydrogen atom. This is in sharp contrast with the weak binding observed for the dimer cation produced in the *direct* reaction of cyanoacetylene cation with cyanoacetylene, a dimer that dissociates easily to regenerate the cyanoacetylene cation. These experimental findings led us to carry out a theoretical study of the $C_6N_2H_2^{+\cdot}$ potential energy surface in which we discovered that the lowest energy isomers are cyclic cations, with the 1,2- and 1,3-dicyanocyclobutadienyl cations having almost identical energies. A hydrogen-bonded linear dimer is also at a minimum, approximately 40 kcal mol^{-1} higher in energy, and this presumably is the weakly bound adduct formed by the direct addition of cyanoacetylene cation to cyanoacetylene.

The loss of either H atom or CN radical from the stable dimer synthesised at C_{60}^{2+} prompted us to

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Dedicated to the memory of Professor Robert R. Squires.

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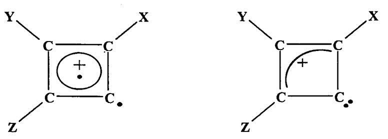

1 2

Diagram 1.

ponder the likely structure of the dissociation products, cyclic ions **1** and **2**. Loss of a group from one carbon atom by homolytic bond fission should, in principle, result in formation of a triplet ion, **1**. This could undergo intersystem crossing to form the singlet ion, **2**, and in a previous investigation of $C_4H_3^+$, the cyclic ion was indeed found to be a singlet [2]. On the $C_4H_3^+$ potential energy surface this ion has the third best energy and is 26 kcal mol^{-1} above ion $H_2C{=}C{=}C{=}C{-}H^+$, the structure at the global minimum.

Unlike in the situation with biradicals reported recently by Squires and co-workers [3], CH_2 has a triplet ground state. This is 9.02 kcal mol^{-1} lower in energy than the singlet [4]. High level ab initio molecular orbital calculations have reproduced this number accurately [5–10]. Carbenes are electron-deficient molecules and replacement of a hydrogen atom by a substituent that is capable of functioning as a π-donor, e.g. F, Cl, NH_2, OH, etc. stabilises the singlet carbene relative to the triplet [10–12]. Ion **2** also contains a π system in conjugation with the formally vacant *p* orbital at the carbene centre, but the π system also formally carries the positive charge and is therefore not expected to be an effective π donor. In fact ion $C_4H_3^+$ was found to be puckered with a barrier to inversion through the planar structure of 29.6 kcal mol^{-1} [2], indicating that π delocalisation is not a factor in stabilising the singlet. Recently we have carried out an extensive study of the $C_4H_5^+$ potential energy surface and found that protonated cyclobutadiene, c-$(CH)_3CH_2^+$, is surprisingly stable and has the next to best energy on the surface [13]. This ion also is puckered and its stability is attributed to *homoaromaticity* [14,15], a concept introduced by Winstein to rationalise the unusual stability of molecules in which possible aromatic conjugation is interrupted by one or more sp^3 hybridised carbons or other saturated groups [15–17].

In neutral molecules the cyano group usually functions as both a σ- and a π-electron-withdrawing substituent. However, when CN is adjacent (α) to a cationic carbon, it can function as a π-donor providing electron density to the formally “vacant” *p*-orbital [18,19]. Despite this reversal in π-donating character, CN is a destabilising substituent in all carbocations [18–21]. Pertinent to the c-$C_4H_n(CN)_{(3-n)}^+$ ions being studied here, the cyano group is strongly destabilising in allyl cations, with the amount of destabilisation being almost independent of the site of attachment [21]. (The 2-cyanoallyl cation is only 2.4 kcal mol^{-1} above the 1-cyanoallyl cation at HF/6-31G(*d*) [21]). Also, the cyclopropenyl cation, a 2π-aromatic system, is destabilised by π donors. On the basis of hydride transfer reactions, the cyano group was found to destabilise the cyclopropenyl cation by 25.7 kcal mol^{-1}, the largest destabilisation of a carbocation recorded for the cyano group [20].

In the current work we examine the structures of c-C_4XYZ^+ ions, where X, Y, and Z are different combinations of H and CN groups. In particular, we are interested in whether these ions have singlet or triplet ground states. Also we are interested in how the substitution of CN groups for H at the α- and β-positions affects the barrier to inversion in the singlet ions.

2. Computational methods

All molecular orbital calculations were performed using GAUSSIAN 98 [22]. Structure optimisations were carried out using the density functional theory (DFT) hybrid method at the B3LYP level [23,24]. The 6-31+G(*d*) basis set [25,26] was used for all structure optimisations. All critical points were characterised by harmonic frequency calculations [27] and in some examples the planar transition structures were shown to collapse to puckered ions by using Intrinsic Reaction Coordinate calculations [28]. The total electronic energies from these calculations are given in Table 1.

Table 1
Total electronic energies (Hartrees), zero-point and thermal energies (both in kcal mol^{-1}) for c-C_4XYZ

Substituents (X, Y, Z)	Electronic energy (Rel)[a]		Zero-point	Thermal
Singlets				
H, H, H	(a) puckered(C_s)	−153.738 26 (0)	31.0	2.2
	(b) planar(C_{2v})	−153.691 41 (29.1)	30.9	2.0
H, CN, H	(a) puckered(C_s)	−245.956 53 (0)	30.2	3.3
	(b) planar(C_{2v})	−245.912 18 (27.3)	29.9	3.1
CN, H, H	(a) puckered(C_1)	−245.954 87 (0.8)	30.0	3.3
	(b) planar(C_s)	−245.920 49 (22.1)	29.9	3.1
CN, CN, H	(a) puckered(C_1)	−338.172 68 (0.7)	29.2	4.4
	(b) planar(C_s)	−338.141 33 (19.8)	28.9	4.1
CN, H, CN	(a) puckered(C_s)	−338.173 61 (0)	29.1	4.4
	(b) planar(C_{2v})	−338.148 92 (15.0)	28.8	4.2
CN, CN, CN	(a) puckered(C_s)	−430.391 46 (0)	28.2	5.6
	(b) planar(C_{2v})	−430.369 81 (12.9)	27.9	5.2
Triplets (all have C_s symmetry)				
H, H, H		−153.706 99 (19.5)	30.7	2.4
H, CN, H		−245.929 88 (16.7)	30.1	3.4
CN, H, H		−245.932 64 (13.9)	29.9	3.4
CN, CN, H		−338.155 81 (10.6)	29.2	4.4
CN, H, CN		−338.156 46 (10.8)	29.1	4.4
CN, CN, CN		−430.379 42 (8.3)	28.3	5.5

[a] Relative energies are in kcal mol^{-1}.

3. Results and discussion

3.1. Geometric parameters for ions in triplet states

At B3LYP/6-31+G(d) the ground electronic state of neutral cyclobutadiene is a singlet that optimises to a rectangular structure with bond distances of 1.338 and 1.577 Å, essentially double and single bonds, respectively. This molecule has been the subject of extensive computation and it has been found to be necessary to include electron correlation in order to establish that the singlet has a lower energy than the triplet state [29–33]. Removal of one π-electron yields the radical cation $C_4H_4^{+\cdot}$ and B3LYP/6-31+G(d) calculations give this ion also to be rectangular, with bond distances of 1.381 and 1.506 Å. This ion has been the topic of two previous high level theoretical studies [34,35] and RMP2/6-31G($2d,p$) calculations gave almost identical bond lengths to our DFT results (1.380 and 1.500 Å [35]). Removal of a hydrogen atom from $C_4H_4^{+\cdot}$ generates the triplet ion, **1**, and this ion has very similar structural parameters to those calculated for $C_4H_4^{+\cdot}$ (Fig. 1). It is planar and

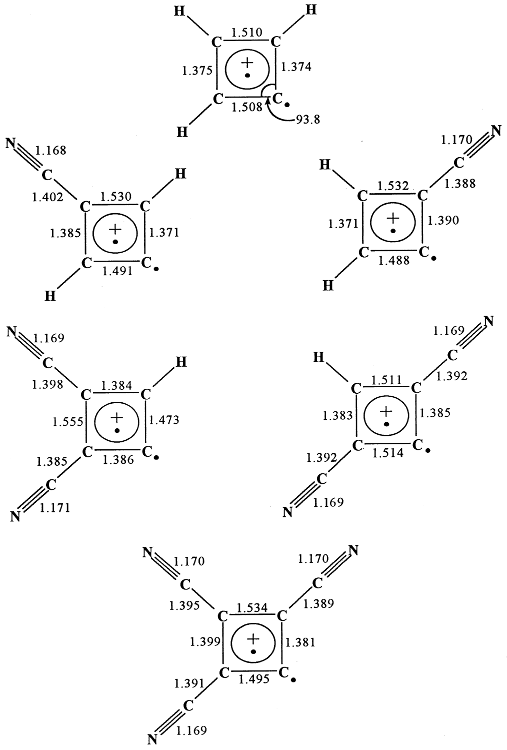

Fig. 1. Structures of c-$C_4H_n(CN)^+_{(3-n)}$ in their triplet states as optimised at B3lYP/6-31+G(d). Bond lengths are in angstroms and the bond angle is in degrees.

essentially a parallelogram, with angles of 93.8° and 86.2°. Unlike in $C_4H_4^{+\cdot}$ and in singlet $C_4H_3^+$ this ion does not pucker, although the lowest vibrational motion is for puckering ($\nu = 322\ \mathrm{cm}^{-1}$).

All the triplet state ions given in Fig. 1 are planar. Substitution of H atoms by CN groups results in elongation of all C–C bonds where one of the carbons is attached to a CN group. The bond between two carbons both carrying CN substituents are the longest. The bond angle within the ring at the carbene carbon is essentially unaffected by substitution and varies between 93.8°, when X = Y = Z = H, and 95.2° when X = Y = CN and Z = H. For this reason we have not included angles on all the structures.

In all the cyano-substituted ions the CN group carries some negative charge and this is attributed to the high electronegativity of the nitrogen atom. However, in these cations they are less negatively charged than CN groups in neutral organonitriles and hence the cyano groups can be considered to carry some of the positive charge on all the c-$C_4H_n(CN)_{(3-n)}^+$ ions. They are more effective at doing this when they are in the α-position relative to the carbene centre and this is reflected in shorter C–CN distances for groups adjacent to the carbene carbon.

The parent triplet ion, $C_4H_3^+$, has one unpaired electron in the σ-system, almost completely localised at the carbene centre (the calculated total atomic spin density on the carbene carbon is $1.03e$). The other unpaired electron is in the π system and is largely located on the two carbons adjacent to the carbene centre (spin densities are $0.400e$ on each α carbon and $0.170e$ on the β carbon). In this respect the π-system of the triplet state of $C_4H_3^+$ resembles an allyl radical. Substitution of an α-H atom by CN results in some delocalisation of the unpaired π-electron spin onto the nitrogen atom, with the majority of it being withdrawn from the unsubstituted α carbon.

3.2. Geometric parameters for ions in singlet states

The parent $C_4H_3^+$ ion, **2** with X = Y = Z = H, has a puckered ring structure with an out-of-plane angle, ϕ, of 51.4° (for definition of ϕ, see structure **3**). The CH–CH bond distances in this ion of 1.403 Å are longer than those calculated for the allyl cation (1.371 Å at HF/3-21G [20]) and the HC–C: bonds of 1.445 Å are shorter than those in dimethylcarbene (calculated to be 1.479 Å at MP2/6-31G(d) [36]). Our geometries are similar to those reported previously at HF/6-31G(d), where CH–CH was calculated to be 1.381 Å and HC–C: to be 1.449 Å [2]. The cross–ring distance between CH groups is 1.793 Å, too long for a formal C–C single bond, but the Wiberg bond index [37] between these two carbons is 0.436, indicative of considerable interaction. These compare with a cross–ring distance of 1.735 Å and a Wiberg bond index of 0.450 in the homocyclopropenyl cation c-$(CH)_3CH_2^+$ [14]. The other Wiberg bond indices in **2** are 1.255 for HC–CH and 1.189 for :C–CH, indicating strong bonding. From the natural population analysis the charge on the carbene centre is $+0.188e$.

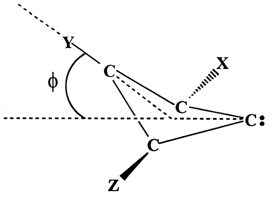

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Diagram 2.

For $C_4H_3^+$ in its singlet state inversion occurs through a planar structure (symmetry C_{2v}). The major structural change in this inversion is an increase in the :C–CH bond distance from 1.445 to 1.514 Å. The bond angle at the carbene centre is least affected, changing from 76.2° to 81.8°. In going from the puckered ring to the planar structure, the other angle changes are from 88.9° to 94.5° for :C–CH–CH, and from 79.4° to 89.2° for HC–CH–CH.

Substitution of H atoms by CN groups does not produce major structural changes. One of the more obvious results is elongation of the adjacent bonds in the ring and this is more pronounced when there is more than one CN group in the ring (Fig. 2). The angle at the carbene centre also increases with increased substitution by CN and this is probably because the ions at the minima are more like the planar ions (the pucker angle decreases from 51.4°

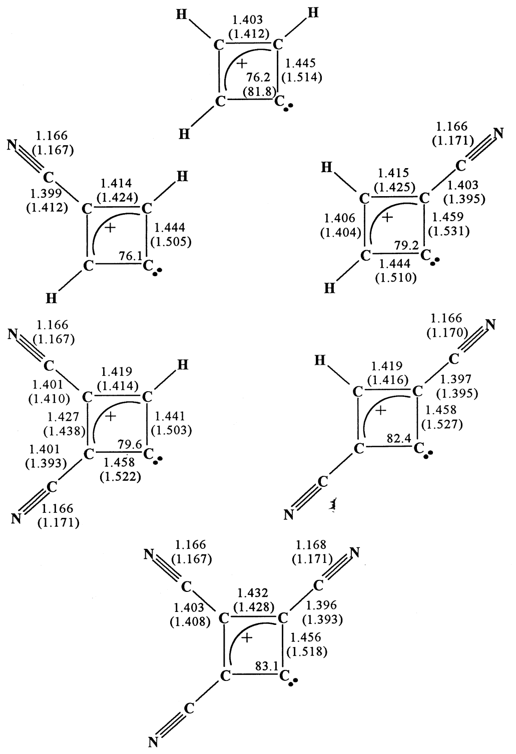

Fig. 2. Structures of $c\text{-C}_4\text{H}_n(\text{CN})^{+}_{(3-n)}$ in their singlet states as optimised at B3LYP/6-31+G(d). Numbers in brackets are for the planar singlet ions. Bond lengths are in angstroms and bond angles are in degrees.

when X = Y = Z = H to 43.4° when X = Y = Z = CN). In the planar ions there is a small decrease in the C–CN bond distance and a slight increase in the C–N distance in the α-substituted ions and it is tempting to attribute this to π-delocalisation of the charge onto the CN group. However, examination of the Mulliken charges showed the CN group in the planar ion to have a larger net-negative charge ($-0.463e$) than in the puckered ion (charge $-0.243e$).

3.3. Barriers to inversion in singlets

As noted in the discussion on structural parameters of the singlets, the CN groups delocalise some of the positive charge and this results in a smaller pucker angle. The calculated barriers and pucker angles are given in Table 2. The effects seem to be almost additive. A CN group adjacent to the carbene centre reduces the barrier to inversion by approximately 7 kcal mol^{-1} whereas one substituted on the opposite carbon reduces it by only about 2 kcal mol^{-1}.

Table 2
Pucker angle and barriers to inversion in singlet c-C$_4$XYZ

Substituents (X, Y, Z)	Barrier to inversion (kcal mol^{-1})	Pucker angle (deg)
H, H, H	29.1	51.4
H, CN, H	27.4	50.4
CN, H, H	21.3	. . .
CN, CN, H	19.1	. . .
CN, H, CN	15.0	45.4
CN, CN, CN	12.9	43.4

From a Natural Orbital Analysis the majority of the positive charge in the parent ion is carried by the hydrogen atoms. All three carbon atoms bearing hydrogens have very small negative charges ($-0.072e$ on the α carbons and $-0.044e$ on the β carbon), but the carbene carbon carries a charge of $+0.188e$, i.e. in the puckered ion the carbene carbon assists in carrying the positive charge. In the planar ion, the transition state to inversion, there is a slight *negative* charge on the carbene carbon, the hydrogens carry approximately the same charge as in the puckered ion, and the charges on the α-carbons are much larger, i.e. the π-system of the planar ion is similar to that of an allyl cation. The net effect of making the ion planar is to decrease the delocalisation of the charge away from the carbene carbon. This reduction in delocalisation results in the large barrier to inversion.

In all ground state singlet ions α-CN groups have smaller negative charges than β-CN groups, indicating that the α substituents interact more extensively with the positive charge. Examination of the α-cyano-substituted ion, **3** with X = Y = H, Z = CN, showed that on going from the puckered ion to the planar transition state the negative charge on the CN group *increases* by $\sim 0.220e$, i.e. the CN group is less effective at delocalising the charge in the planar ion than in the puckered ion. Nevertheless, in this planar ion the C$_\alpha$–CN collection of atoms carries slightly more positive charge ($+0.723e$) than the C$_\alpha$–H

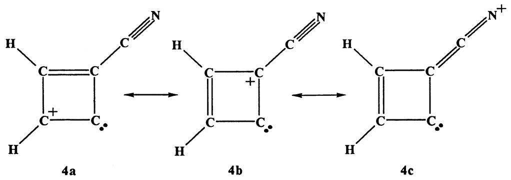

Diagram 3.

group ($+0.678e$) and together these groups accommodate all the positive charge. This is consistent with the ion being represented by resonance structures **4a**, **4b**, and **4c**, with **4a** being the dominant one.

Substitution of a second CN group on the other α carbon has the dramatic effect of producing positive charges on both CN groups in the planar ion, thereby delocalising $\sim+0.300e$ onto the cyano groups, compared with a charge of $-0.460e$ on these two groups in the puckered ion. This effect is amplified further in the tricyano-substituted ion where the combined charge on the two α-CN groups is $+0.600e$ in the planar ion compared with $-0.370e$ in the puckered ion.

3.4. Singlet/triplet splitting

The singlet state of the unsubstituted ion, $C_4H_3^+$, is 19.5 kcal mol^{-1} lower than the triplet. Introducing CN substituents reduces this difference, but even the triply substituted ion has a singlet ground state, 8.3 kcal mol^{-1} lower than its triplet state (Table 3). The stability of the singlet states for these ions is attributed to the stabilisation afforded by homoaromaticity in the puckered singlet. Comparison of the triplet states with the planar singlets permits an examination of substituent effects without the complication of homoaromaticity. For the parent ion, $C_4H_3^+$, the triplet state is 9.6 kcal mol^{-1} lower than the planar singlet, almost the same energy difference as in CH_2. Substitution by a CN group adjacent to the carbene centre lowers the energy of the planar singlet relative to that of the triplet, whereas a CN on the β-carbon atom raises the relative energy of the planar singlet. This can be understood in terms of the CN group stabilising the singlet preferentially over the triplet when it is located adjacent to the carbene centre. This is consistent with the differences in geometric parameters discussed previously.

Table 3
Energies of singlets relative to triplets (kcal mol^{-1}) for c-C_4XYZ[a]

Substituents (X, Y, Z)	Puckered singlet	Planar singlet
H, H, H	−19.5	9.6
H, CN, H	−16.7	10.6
CN, H, H	−13.9	7.4
CN, CN, H	−10.6	8.5
CN, H, CN	−10.8	4.2
CN, CN, CN	−8.3	4.6

[a] A negative number indicates that the singlet has better energy.

4. Conclusions

c-$C_4H_3^+$ is electron deficient both because it carries a positive charge and also because it has a carbene centre. The parent carbene, CH_2, in its ground state is a triplet, but the singlet state can be stabilised by replacing a hydrogen by a substituent that is a π-donor. The π-system in c-$C_4H_3^+$ is a poor candidate to stabilise the singlet carbene as this is formally the location of the positive charge. Nevertheless the singlet state is heavily stabilised and this is coupled with a large out-of-plane angle that reduces the conventional π-delocalisation, but increases the cross–ring interaction necessary to promote formation of a 2π-aromatic cyclopropenyl cation.

The CN group is always destabilising in carbocations and in the c-$C_4H_n(CN)^+_{(3-n)}$ ions the effect is larger in the ions in the singlet states; consequently the effect of substitution by CN is to reduce both the singlet/triplet splitting and to reduce the barrier to inversion in the singlet.

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