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THE CALCULATED ACIDITY OF BENZOCYCLOPROPENE AND ITS RELEVANCE TO THE EASE OF BASE CLEAVAGE OF 1-TRIMETHYLSILYLBENZOCYCLOPROPENE

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Summary

STO-3G calculations indicate that benzocyclopropene is substantially more acidic than toluene, in line with the previously reported ease of base cleavage of 1-trimethylsilylbenzocyclopropene and ease of metallation of benzocyclopropene; the calculated pK_a value of 33 compares with the value of 36 derived from the cleavage data. The corresponding calculations for cyclopropene indicate a very low acidity, comparable with that of ethane. The higher acidity of benzocyclopropene than of toluene appears to be associated with a high polarizability of the C—C bonds between the carbanionic centre and the adjacent carbon atoms of the aromatic ring; the large σ-charge thus placed on the latter carbon atoms in the carbanion is compensated by delocalization of π-charge away from these centres. The corresponding C—C bonds of the cyclopropenyl anion are similarly polarized, but in this case there can be no compensating delocalization of π-charge.

Introduction

The base cleavage of 1-trimethylsilylbenzocyclopropene by MeONa—MeOH was recently found to be substantially faster than that of benzyltrimethylsilane, implying a higher acidity for benzocyclopropene than for toluene [1]. The cleavage data suggested a pK_a of about 36 for benzocyclopropene compared with 41 for toluene *. In the same study, benzocyclopropene was observed to be readily metallated by n-butyllithium at low temperature, which is also consistent with a fairly high acidity. Such an acidity was somewhat surprising in the light of the very low acidity of cyclopropene at the methylene position (acidities even lower than that of methane have been estimated for

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* All the solution pK_a's in this paper refer to ion-pair acidities in $CsNHC_6H_{11}$—$C_6H_{11}NH_2$ [2].

some simple trialkylcyclopropenes [3]), which has been attributed in part to anti-aromaticity of the 4-electron system [4]. (The arguments in support of anti-aromaticity have recently been questioned, however [5]). Consequently we undertook molecular orbital calculations on cyclopropene, benzocyclopropene, and their anions, and the results are presented and discussed below. Some calculations on the cyclopropenyl anion were carried out some years ago by Clark [6], but these have recently been criticized [5].

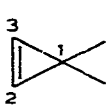
Method and results

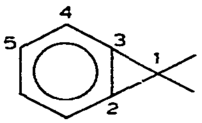
Central to the calculations was the question of the geometry around the carbanion centres. We chose to fix the C—H distance(s) at 112 pm, but to attempt to optimize the R—C—H angle(s). This is not straightforward, since it has previously been found that optimization of angles at a carbanion centre using a minimal basis set leads to angles which are clearly too small [7]. If a double ζ (4-31) set is used, however, the angles obtained for CH_3^- are in close agreement with those calculated using a large basis set with extensive configuration interaction [7] *. Unfortunately, calculations at this level are not possible for the anions from toluene and benzocyclopropene using the version of Gaussian 70 available to us, because the basis sets are too large. We thus explored the effect of using a "mixed" basis set consisting of the standard STO-3G basis on all atoms except the carbanionic carbon along with a 4-31 basis of this atom only. This proved to be tedious, as only with very careful damping was it possible to make the calculations converge, but we nevertheless carried the procedure to completion. When tested with the $CH_2{=}CHCH_2^-$ ion, the C—C—H angle at the carbanion centre was calculated to be 114.0° using the mixed basis set compared with a value of 113.1° using the complete 4-31 basis. Similar agreement was previously obtained for carbanions without π-electron systems [7].

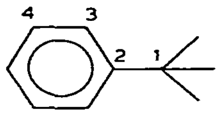
The remaining geometrical parameters were not allowed to change on going from the conjugate acid to the anion.

For calibration purposes, calculations were also carried out on cyclopentadiene and its anion.

The (non-standard) numbering of carbon atoms in the account below is shown for the parent hydrocarbons in the following diagrams.







The "experimental" geometry [9] used for the cyclopropene system was as follows: C(1)—C(2), 151.5 pm; C(2)—C(3), 130 pm; C(1)—H, 108.7 pm; C(2)—H 107 pm; C(2)—C(1)—H, 119.16°; C(2)—C(3)—H, 149.9°.

The "experimental" geometry for benzocyclopropene was based on averages

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* Radom has shown that the 4-31 basis is satisfactory for the geometry of negative ions, and the STO-3G basis less so [8].

of (very similar) values for two substituted compounds [10], and was as follows: C(1)—C(2), 150 pm; C(3)—C(4), 140 pm; C(4)—C(5), 141 pm; C(1)—H, 112 pm; arylC—H, 108 pm; C(2)—C(1)—H, 119.6°; C(1)—C(2)—C(3), 67.47°; C(2)—C(3)—C(4), 127°; C(3)—C(4)—H, 126.23°; C(4)—C(5)—H, 117.27°; C(3)—C(4)—C(5) (and other CCC benzene ring angles) 107.54°.

For the "standard" geometry [11] in the case of benzocyclopropene, the benzene ring was taken to be a regular hexagon with C—C 139.7 pm, arylC—H, 109 pm, and C(1)—H, 151 pm.

For toluene the parameters used were: ring C—C, 140 pm; C—H, 109 pm; C(1)—C(2), 152 pm; all angles 120° or 109.47° as appropriate.

The experimental geometry was used for cyclopentadiene [12].

The optimized C(2)—C(1)—H angles in the carbanions were as follows: benzyl, 115.9°; cyclopentadienyl, 128.5°; cyclopropenyl, 108.2° (the deviation of the C—H bond from the plane of the ring is 69.8°); benzocyclopropenyl, 115.1° ("experimental" geometry) or 114.3° (standard geometry) (the corresponding out of plane angles are 61.6 and 62.3°, respectively).

The calculated energies are shown in Table 1, and charge densities and Mulliken overlap populations in diagram form. To convert the energy differences, ΔE, between the parent hydrocarbons and the anions into pK_a values, it is assumed that $\Delta E(\mathrm{RH}) - \Delta E(\mathrm{PhCH_3})$ is proportional to ΔpK_a, where $\Delta pK_a = pK_a(\mathrm{PhCH_3}) - pK_a(\mathrm{RH})$. Thus the value of 0.070467 a.u. for $\Delta E(\mathrm{RH}) - \Delta E(\mathrm{PhCH_3})$ for RH = cyclopentadiene corresponds with a ΔpK_a of 26, and the other pK_a's can then be derived, with the results shown in the Table.

It will be seen that the energy calculated for benzocyclopropene is lower with the experimental than with standard geometry, as expected. The opposite is true, for the anion, implying that a pK_a value of <33 would be derived if the geometry of the anion were fully optimized. If the calculated energy for the benzocyclopropene based on the experimental geometry is used along with the energy for the anion based on standard geometry (with optimized geometry at the anionic centre as usual), a value of 30.5 is derived.

We should note that in all the calculations the eigenvalue of the highest

TABLE 1

CALCULATED ENERGIES AND DERIVED pK_a VALUES

RH	Basis [a]	$-E$(RH) (a.u.)	$-E(\mathrm{R}^-)$ (a.u.)	ΔE (a.u.)	pK_a [b] (calc.)
cyclopentadiene	STO-3G	190.454773	189.700921	0.753852	15
	4-31	192.512311	191.882376	0.629935	
benzocyclopropene	STO-3G(EG) [c]	265.175158	264.371464	0.803694	33
	STO-3G(SG) [d]	265.167653	264.379280	0.788373	28
toluene	STO-3G	266.474070	265.649751	0.824319	41
cyclopropene	STO-3G	114.399435	113.523560	0.875875	60
	4-31	115.641713	114.899598	0.742115	
ethane [e]	STO-3G			0.885423	63.5
	4-31			0.738034	

[a] With optimized angles for the anions (see text). [b] Based on ion-pair values for toluene and cyclopentadiene in $\mathrm{CsNHC_6H_{11}/C_6H_{11}NH_2}$ [2]. [c] Experimental geometry. [d] Standard geometry. [e] Eclipsed conformation; see ref. 7.

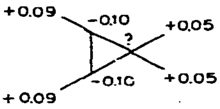
Charge Distributions

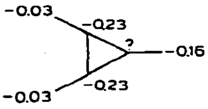
Cyclopropene

Parent hydrocarbon

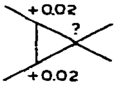
Anion

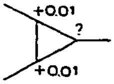
σ-charge



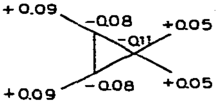


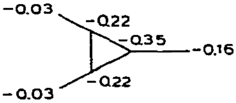
π-charge





Total charge

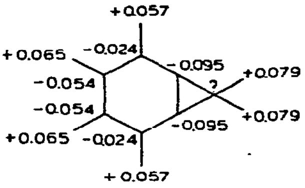




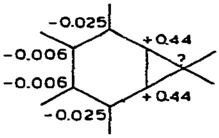
Benzocyclopropene

Parent hydrocarbon

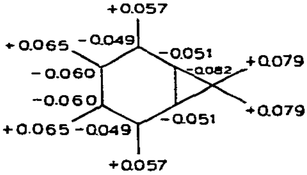
σ-charge



π-charge



Total charge



Benzocyclopropene

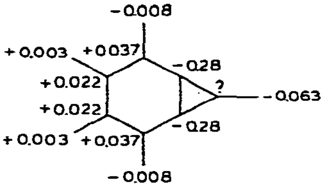
Anion

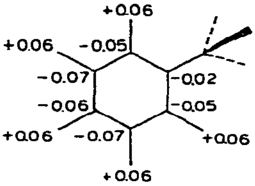
Toluene

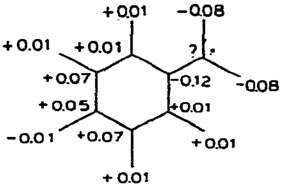
Parent hydrocarbon

Anion

σ-charge







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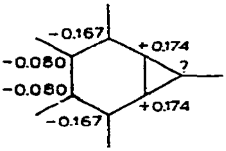
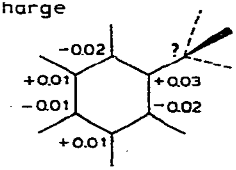
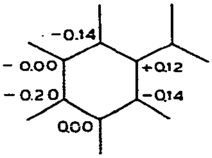
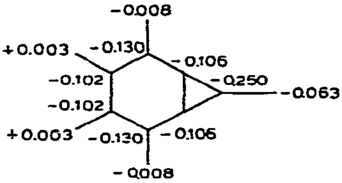
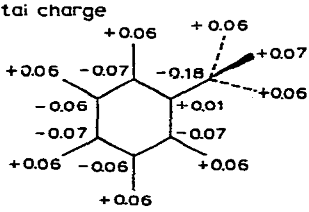


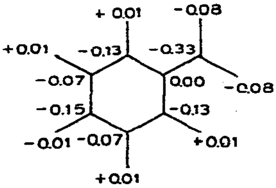


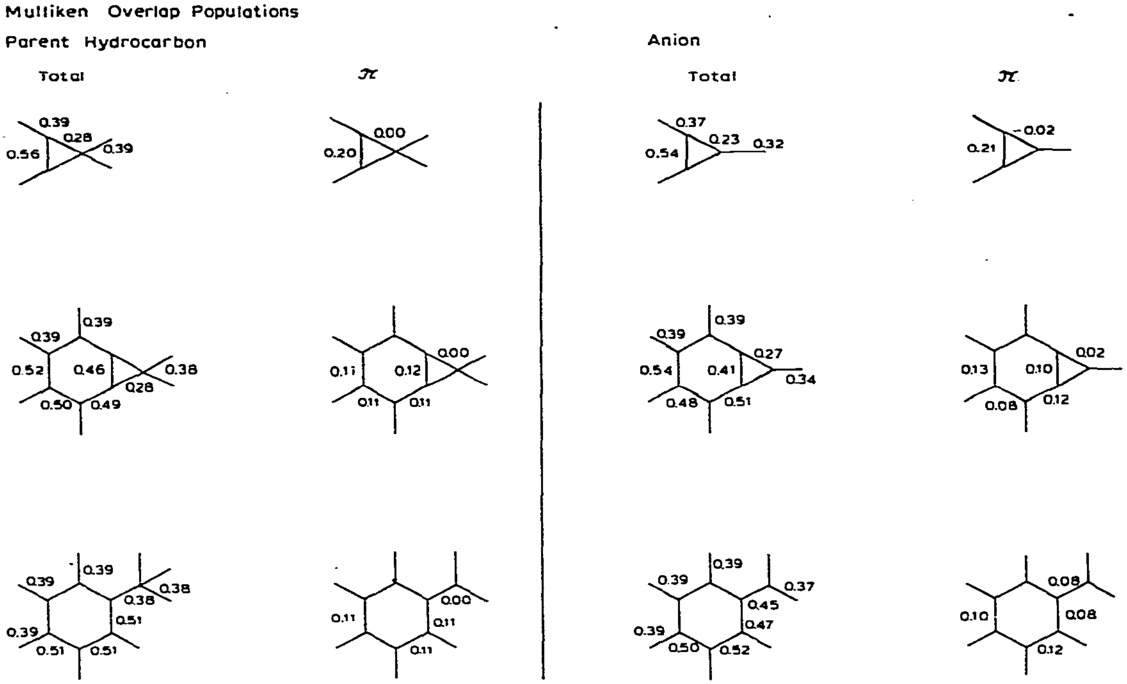


Total charge









occupied orbital in the anion is positive, implying an unbound state. This is commonly the case in ab initio calculations on negative ions, and they have been criticized on these grounds by Ahlrichs [13]. However, Radom has shown that, in spite of this, good agreement with experimental geometries can be obtained in practice for SCF calculations [8]. It appears that SCF calculations with small basis sets parallel the exact solutions for negative ions, in a way similar to that well recognised for positive ions and neutral species, and thus that our interpretations, based on relative effects in the various systems, are empirically valid.

Discussion

The calculated pK_a values, while necessarily only approximate, indicate that benzocyclopropene is substantially more acidic than toluene; the pK_a calculated on the basis of "experimental" geometry is 33, and this compares with the value of 36 derived from the rate of base cleavage of the 1-trimethylsilyl-derivative [1]. There thus seems no reason to doubt the validity of the conclusions reached on the basis of the cleavage data.

It is noteworthy that the value of the coupling constant $^1J(^{13}C—H)$ for the C(1)—H bonds in benzocyclopropene, viz. 1740 Hz [14], (corresponding to 34% *s*-character in the bond) would imply an acidity close to that of benzene (pK_a ca. 43 [15]) in the absence of any specific electronic stabilization of the charge in the anion. We shall see below that the charge at the carbanion centre is, in fact, substantially delocalized on to the carbon atoms of the fused benzene ring.

As expected, the calculations indicate a very low acidity for cyclopropene, giving a pK_a of 60, close to that, viz. 63.5, calculated for ethane.

The other features of interest in the results of the calculations, with some comments, are as follows.

(a) The optimized CCH angle at the carbanionic carbon atom, C(1), in the cyclopropenyl (108°) is smaller than that in the benzyl anion (116°), and very close to that indicated by Clark's calculations [6]. The calculated angle for the benzocyclopropenyl anion (115°) is, however, close to that for $PhCH_2^-$. The difference between the cyclopropenyl and benzocyclopropenyl anions can be associated with a much smaller repulsion between the lone pair and the π-electrons of the C(2)—C(3) bond in the latter ion.

(b) The total charge on the anionic carbon atom of the benzocyclopropenyl anion is significantly smaller than the corresponding charge in the benzyl anion, in keeping with the higher acidity of benzocyclopropene. The detail of the dispersal of the charges is instructive and it will be seen that the striking difference between the charge distributions on the two cases lies in the markedly greater charge (—0.11) on each of the ring carbon atoms joined to the carbanionic centre in the benzocyclopropenyl anion than on the corresponding ring carbon atom of the benzyl anion (0.00).

(c) A substantial degree of overall negative charge is located at the C(2) and C(3) carbon atoms of the benzocyclopropenyl anion in spite of the large positive π-charge there (viz. +0.17, compared with the value of +0.12 on the single corresponding atom in $PhCH_2^-$). This is because of the very large negative σ-charge on each of these atoms (viz. —0.28, compared with —0.12 on the single corresponding atom in $PhCH_2^-$). The total π-charge on the ring carbon atoms in the benzocyclopropenyl anion (—0.15) is substantially smaller than that in $PhCH_2$ (—0.36), and the greater dispersal of the charge from the carbanionic centre in the benzocyclopropenyl anion than in $PhCH_2^-$ is primarily the result of the much greater induction of the electrons of the $C—C^-$ σ-bond towards the ring carbon atoms.

(d) A similar large induction occurs along the corresponding bonds in the cyclopropenyl anion, but in this case there can be no delocalization of the π-electron away from the C(2) and C(2) carbon atoms to compensate for the large σ-charge. The much greater stability of the benzocyclopropenyl than of the cyclopropenyl anion is clearly to be associated with the delocalisation of π-electrons away from the C(2) and C(3) carbon atoms to the other ring carbon atoms. The large difference between the CCH angles at the carbanion centres of the cyclopropenyl and benzocyclopropenyl anions is also to be associated with this delocalization.

The large σ-delocalization of the charge in the anions from cyclopropene and benzocyclopropene can be associated with the weakness of the C(1)—C(2) and C(1)—C(3) bonds resulting from the poor orbital overlap in these highly strained structures. In other words, electrons are easily removed from the highest occupied orbital.

(e) The Mulliken overlap population of the C(1)—C(2) bonds, which, of course, increases (by 0.07) on going from $PhCH_3$ to $PhCH_2^-$, decreases by a small amount (0.01) on going from benzocyclopropene to its anion, and by a more substantial amount (0.05) on going from cyclopropene to its anion. In the anions the total overlap populations in these bonds are 0.45, 0.27 and 0.23, respectively. The π-overlap population in the bonds has a value of +0.08 for $PhCH_2^-$, a small but positive value, +0.02, for the benzocyclopropenyl anion and a small negative value, —0.02, for the cyclopropenyl anion. The small positive value for the benzocyclopropenyl anion is consistent with the transmission of a small amount of π-charge (—0.15) into the 6-membered ring. The negative value for the cyclopropenyl anion would be consistent with antiaromaticity, but it is likely, as pointed out by Bauld and his colleagues [5], that the negative overlap density would disappear if configurational interaction were taken into account.

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