PERKIN 2
KEYNOTE

Synthesis and characterization of the negative ion of non-Kekulé benzene

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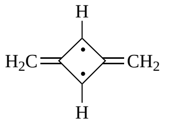
The 2,4-dimethylenecyclobutane-1,3-diyl negative ion 2 has been generated in the gas phase from the reaction of atomic oxygen anion with 1,3-dimethylenecyclobutane 3. This negative ion is the necessary precursor for photoelectron spectroscopic measurements of the singlet–triplet splitting in the corresponding neutral biradical 1. Gas-phase ion–molecule reactions involving several different electrophiles, radical traps and Brønsted acids were used to identify the structure of ion 2, and to rule out the presence of other $C_6H_6^{\bullet -}$ isomers. Ion 2 displays characteristic radical- and carbanion-type reactivity, including adduct formation with NO, COS and CO_2, S-atom abstraction from CS_2, and thiomethyl group abstraction from CH_3SSCH_3. The proton affinity of radical anion 2 was determined from acid–base bracketing experiments to be 383.3 ± 2.0 kcal mol^{-1}. The gas-phase acidity of hydrocarbon 3 was determined by bracketing to be 366.7 ± 3.0 kcal mol^{-1}, while the proton affinity of its conjugate base carbanion 7 was bracketed at 369.2 ± 2.0 kcal mol^{-1}. The 2.5 kcal mol^{-1} difference is interpreted as evidence for protonation of the dienylic anion moiety in 7 at one of the exocyclic methylene groups to give 1-methyl-3-methylenecyclobutene as the lower energy C_6H_8 tautomer. The electron affinities of biradical 1 and the corresponding monoradical 2,4-dimethylenecyclobutyl 9 were measured by a kinetic method involving collision-induced dissociation of SO_2 adducts of ions 2 and 7. The biradical and monoradical were found to have identical electron affinities (EA), 26.3 ± 0.2 kcal mol^{-1} (1.14 ± 0.01 eV). Density functional calculations of the structures and energies of 1, 2 and several related species were carried out at the B3LYP/6-31+G* level. Good agreement was achieved between the experimental thermochemistry and the predicted energetics based on isodesmic reactions. The experimental and theoretical thermochemistry reveal a dramatic deviation from CH bond energy additivity in forming triplet biradical 1 from hydrocarbon 3 by a hypothetical sequence of CH bond dissociations: the second ring CH bond strength is 16.6 ± 3.6 kcal mol^{-1} stronger than the first due to electronic destabilization of the π system in 1 from antiaromaticity.

Introduction

Renewed interest in biradicals[1] has been inspired by burgeoning applications of these species in materials science[2] and drug design.[3] The quest for organic materials exhibiting ferromagnetism has led to numerous studies of certain *non-Kekulé* molecules[4] as models for ferromagnetic coupling units in high-spin organic polymers.[2,5] Among these is 2,4-dimethylenecyclobutane-1,3-diyl **1**. This non-Kekulé isomer of benzene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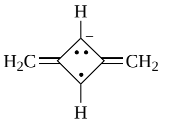
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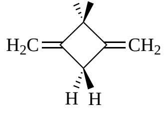
possesses a pair of non-disjoint non-bonding molecular orbitals (NBMO), and it is therefore predictably a triplet biradical.[6] This was confirmed by Snyder and Dougherty[7] in 1985 and by Dowd and Paik[8] in 1986 with the observation of the EPR spectra of **1** trapped in low-temperature matrices. *Ab initio* calculations by Borden, Davidson and co-workers predict the energy splitting between the $^3B_{2u}$ ground state and the lowest singlet state (^1A_g) of **1** to be about 18 kcal mol^{-1}.[9] The singlet–triplet splitting of **1** has not been determined experimentally. The best method for measuring this quantity is negative ion photoelectron spectroscopy (NIPES).[10] This experiment requires intense beams of the negative ion of **1** and, therefore, a rational gas-phase synthesis of 2,4-dimethylenecyclobutane-1,3-diyl anion **2** is needed.

Several different approaches have been used to generate carbene and biradical negative ions for gas-phase reactivity studies and for NIPES experiments. For example, dissociative electron ionization of suitable neutral precursors such as diazo compounds has been used to produce $CH_2^{\bullet -}$[11] and other carbene anions.[12] We recently described a regiospecific synthetic method for generating gaseous negative ions of biradicals and triradicals wherein polysilylated precursors are sequentially desilylated by fluoride ion and molecular fluorine.[13] A common method that has been applied to the synthesis of carbene and biradical negative ions is the 1,*n* (*n* = 1,2,3 . . .) abstraction of $H_2^{\bullet +}$ from hydrocarbons and other organic molecules by $O^{\bullet -}$.[14] For instance, this reaction was used to make *o*-benzyne anion from benzene,[15] vinylidene anion from ethylene,[16] cubene anion from cubane,[17] and tetramethyleneethane anion from 2,3-dimethylbuta-1,3-diene.[18]

In this paper we explore the utility of this latter method for synthesizing **2** from the neutral hydrocarbon 1,3-dimethylenecyclobutane **3**. Four different $H_2^{\bullet +}$ abstraction products (**2**, **4**–**6**) are plausible from the reaction of $O^{\bullet -}$ with **3**. Thermochemical considerations rule out formation of the divinylic radical anion isomer that would result from abstraction of H-atom from one vinylic position and H^+ from the other (Δ*H* is estimated to be about +8 kcal mol^{-1}), whereas biradical negative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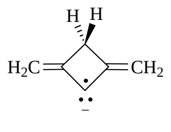

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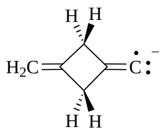

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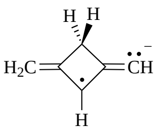

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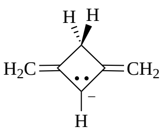
ion **2** and its isomers **4**–**6** are all energetically accessible. We use ion–molecule reactions and tandem mass spectrometry to demonstrate that the structure of the $H_2^{\bullet+}$ abstraction product obtained from $O^{\bullet-}$ + **3** is the desired biradical negative ion **2**. Reactivity comparisons are made with the corresponding even-electron $C_6H_7^-$ carbanion **7**. We also present experimental



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determinations of the proton affinities and electron binding energies of **2** and **7** and the gas-phase acidity of **3**, along with supporting theoretical studies of the thermochemical properties and electronic structures of isomeric $C_6H_6^{\bullet-}$ and $C_6H_7^-$ ions.

Experimental

All experiments were carried out at room temperature (298 ± 2 K) with a flowing afterglow–triple quadrupole apparatus that has been described in detail previously.[19] The flow reactor was pressurized with 0.4 Torr of He buffer gas, with a flow rate of 200 STP $cm^3\ s^{-1}$ and bulk flow velocity of 9700 cm s^{-1}. Atomic oxygen anion, $O^{\bullet-}$, was produced by dissociative ionization of N_2O introduced near the electron emission source located at the upstream end of the flow tube. Fluoride ion was formed by electron ionization of NF_3. Reagent ions formed in the source region are transported through the reactor by the flowing helium, where they are allowed to react with the gaseous neutral reagents introduced *via* leak valves. The ions produced in the flow tube are thermalized to ambient temperature by *ca.* 10^5 collisions with the helium buffer gas. Negative ions are extracted from the flow tube through a 0.5 mm orifice in a nose cone, and then focused into an EXTREL triple quadrupole analyzer for mass spectrometric analysis.

Many of the ion–molecule reactions described in this account were carried out in the gas-tight quadrupole collision chamber (Q2) of the triple quadrupole analyzer. For these experiments, the ion of interest is mass-selected by the first quadrupole (Q1), and then allowed to react with a neutral reagent gas maintained in Q2 at a pressure of *ca.* 0.03–0.20 mTorr. The kinetic energy of the reactant ion is determined by the Q2 pole offset voltage, which is maintained near 0 V for examining exothermic reactions. For collision-induced dissociation (CID) experiments, collision energies of 20–25 eV (lab-frame) were used with Ar target gas pressures of 0.03–0.06 mTorr. Product ions and parent ions are extracted from Q2 with an electrostatic lens into the third quadrupole (Q3), where they are mass analyzed and then detected with an electron multiplier.

For the electron affinity determination, CID of the RSO_2^- ions was carried out with use of a (lab-frame) collision energy of 23 eV and an Ar target pressure of 0.035 mTorr. The reported $R^-/SO_2^{\bullet-}$ fragment ion yield ratios represent averages of at least ten replicate measurements. All intensities were recorded using a digital counter operating with a 10 s gate time. The ion intensity measurements follow a Poisson distribution, so the uncertainty in each counter measurement was calculated by taking the square root of the intensity. Uncertainties in the yield ratios were determined by using standard error propagating procedures,[20] and the final uncertainties in the electron affinities were assigned in accordance with the methods described previously.[21]

Ab initio molecular orbital calculations were performed with the GAUSSIAN 94 suite of programs on an IBM RISC/6000 39H computer.[22] The structures and thermochemical properties of **1**–**7** and related species were investigated with density functional theory (DFT). For these calculations, the B3LYP procedure was used in conjunction with a 6-31+G* basis set, *i.e.* B3LYP/6-31+G*. The B3LYP method employs the Becke three-parameter fit to the combined Hartree–Fock and local density approximations for the exchange energy,[23] and the non-local correlation functional given by Lee, Yang and Parr[24] along with the local correlation functional for the homogeneous electron gas. Optimized geometries and total energies were obtained at the B3LYP/6-31+G* level, and normal-coordinate vibrational analysis carried out at this level verified each of the optimized structures to be a true energy minimum. For the thermochemical calculations, the harmonic vibrational frequencies of each molecule were scaled by a factor of 0.972.[25] Listings of the optimized geometries, total energies and vibrational frequencies for all molecules and ions are available as a supplementary publication [SUPP. NO. 57354 (4 pp.) †].

Materials

Gas purities were as follows: He (99.995%), N_2O (99.5%), NO (99%), NO_2 (99.5%), SO_2 (99.98%), O_2 (99%), CO_2 (99.5%), COS (97.5%), NF_3 (98%) and CH_4 (99%). 1,3-Dimethylenecyclobutane was synthesized by modification of the synthesis reported by Roberts and co-workers,[26] in which *m*-chloroperbenzoic acid was substituted for hydrogen peroxide in the amine oxidation step. All other reagents were obtained from commercial sources and used as supplied except for degassing of liquid samples prior to use.

Results and discussion

Reaction of $O^{\bullet-}$ with hydrocarbon **3** yields three primary products, corresponding to $H_2^{\bullet+}$ abstraction [eqn. (1a)], proton

$$C_6H_8\,(\mathbf{3}) + O^{\bullet-} \longrightarrow C_6H_6^{\bullet-} + H_2O \qquad (1a)$$

$$\longrightarrow C_6H_7^-\,(\mathbf{7}) + HO \qquad (1b)$$

$$\longrightarrow C_6H_7 + HO^- \qquad (1c)$$

abstraction giving **7** [eqn. (1b)] and H-atom abstraction [eqn. (1c)]. Hydroxide ion and the $H_2^{\bullet+}$ abstraction product undergo secondary reactions with **3** to produce carbanion **7**. Formation of $C_6H_7^-$ from reaction between $C_6H_6^{\bullet-}$ and C_6H_8 could occur by either proton or hydrogen atom transfer, which would require an isotope-labelling experiment to distinguish. Analysis of the three product ion yields as a function of the hydrocarbon concentration in the flow reactor indicates the primary product distribution to be 43% $C_6H_6^{\bullet-}$, 42% $C_6H_7^-$ and 15% OH^-. This is quite similar to the primary product distribution reported for the reaction of $O^{\bullet-}$ with 6,6-dimethylfulvene.[27]

Ion–molecule reactions and structure analysis

Atomic oxygen is known to react with unsaturated hydrocarbons *via* multiple pathways to give mixtures of isomeric $H_2^{\bullet+}$ abstraction products.[28] Four different $C_6H_6^{\bullet-}$ isomers are feasible from the reaction of $O^{\bullet-}$ with **3**: biradical negative ion **2** and the radical anion **6** from two different 1,3-$H_2^{\bullet+}$ abstractions,

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† For details of the British Library supplementary publications scheme, see 'Instructions for Authors (1998)', on the RSC's Website, URL:http://www.rsc.org/authors. The data are also directly accessible on the RSC's Website on URL: http://www.rsc.org/suppdata/perkin2/1998/1027.

Table 1 Ionic products from gas-phase reactions of $C_6H_6^{\bullet -}$ and $C_6H_7^-$ ions with selected neutral compounds

Compound	$C_6H_6^{\bullet -}$	$C_6H_7^-$ (**7**)
N_2O	No reaction	No reaction
NO	$[C_6H_6NO]^-$	No reaction
NO_2	NO_2^-	NO_2^-
O_2	Signal loss	Signal loss
CH_3SSCH_3	$[C_6H_6SCH_3]^-$, $CH_3SCH_2S^-$, CH_3S^-	$CH_3SCH_2S^-$, CH_3S^-
CO_2	$[C_6H_6CO_2]^{\bullet -}$	$[C_6H_7CO_2]^-$
CS_2	$[C_6H_6S]^{\bullet -}$, $[C_6H_6CS_2]^{\bullet -}$	$[C_6H_7CS_2]^-$
COS	$[C_6H_6S]^{\bullet -}$, $[C_6H_6COS]^{\bullet -}$	$[C_6H_7COS]^-$
SO_2	$SO_2^{\bullet -}$, $[C_6H_6SO_2]^{\bullet -}$	$SO_2^{\bullet -}$, $[C_6H_7SO_2]^-$
D_2O	No reaction	No reaction
MeOD	MeO^-	No reaction
EtOD	EtO^-	No reaction
Pr^iOD	Pr^iO^-	No reaction

and divinylcyclobutylidene carbene **4** and vinylidene carbene anion **5** from two different 1,1-$H_2^{\bullet +}$ abstractions. In principle, the product isomer distributions arising from $H_2^{\bullet +}$ abstraction can be revealed by use of deuteriated neutral precursors. This approach has been used by Grabowski and co-workers to resolve the isomeric product ions formed in reactions of $O^{\bullet -}$ with 6,6-dimethylfulvene[27] and 2,3-dimethylbuta-1,3-diene.[18] However, recent work in our laboratory with other deuteriated hydrocarbons has shown that the relative yields of $H_2^{\bullet +}$, $HD^{\bullet +}$, and $D_2^{\bullet +}$ abstraction are not necessarily reliable indicators of the isomeric product distribution, since H/D exchange between the nascent radical anion and the water molecule can occur within the ion–molecule complex prior to dissociation.[29] For this reason, we have used ion–molecule reactions to identify the structure of the $H_2^{\bullet +}$ abstraction product of eqn. (1a), henceforth referred to as $C_6H_6^{\bullet -}$.

The reactions of both $C_6H_6^{\bullet -}$ and the even-electron carbanion $C_6H_7^-$ (**7**) were examined with a series of neutral reagents that are commonly used as organic anion structure probes.[30] These include open-shell reagents such as NO, NO_2 and O_2, electrophiles such as CO_2 and CS_2, and deuteriated acids such as D_2O and CH_3OD. A summary listing of the products observed from the reactions of both $C_6H_6^{\bullet -}$ and **7** with selected compounds is given in Table 1, and a discussion of this chemistry follows. The interpretation of the observed reactivity in the flow tube can be complicated by isobaric product ion mixtures and by the presence of background reagent gases. Accordingly, many of the ion–molecule reactions described below were examined in both the helium flow reactor and with the mass selected $C_6H_6^{\bullet -}$ and $C_6H_7^-$ ions in Q2 of the triple quadrupole analyzer with minimal reactant ion kinetic energies. When these reactions are performed in Q2, the reactant ion is unambiguously determined and the kinetic energy dependence of the product yield can provide a qualitative indication of the exo- or endo-thermicity of the reaction.

The absence of reaction of $C_6H_6^{\bullet -}$ with N_2O rules out the vinylidene anion structure **5**. Nibbering and Dawson established that N_2O reacts with the parent vinylidene anion $CH_2{=}C^{\bullet -}$ exclusively by nitrogen abstraction to give CH_2CN^-,[31] and nitrogen abstraction is also observed for the related ion $OCC^{\bullet -}$.[32] However, the $C_6H_6^{\bullet -}$ product of eqn. (1a) does not react at all with N_2O, nor does carbanion **7**.

The reactions with the open-shell reagents NO, NO_2 and O_2 and with CH_3SSCH_3 can probe the nature of the radical site in $C_6H_6^{\bullet -}$. NO reacts with $C_6H_6^{\bullet -}$ exclusively by addition but it does not react at all with $C_6H_7^-$ [eqn. (2)]. Addition of NO to

$$C_6H_6^{\bullet -} + NO \longrightarrow [C_6H_6NO]^- \qquad (2)$$

organic radical anions has been observed in our lab[13,33] and others.[18,27] This reaction is usually characteristic of distonic ion structures (ionized biradicals[34]) with formally separate charge and odd-spin sites. Relatively basic, even-electron anions such as phenide,[33] hydride[35] and hydroxide[36] usually react with NO by associative detachment, *i.e.* addition and electron loss. Recent work in our lab[29] has shown that carbene anions, such as $PhCH^{\bullet -}$ also react with NO by associative detachment, presumably due to the large exothermicity ‡ associated with formation of the oximate anion adduct, *e.g.* $[PhCH{=}NO]^-$. Thus, the observation of NO addition to $C_6H_6^{\bullet -}$ without significant total signal loss is inconsistent with oximate anion formation, which would occur if NO added to the divalent carbons of isomers **4** and **6**. The theoretical results and the observed reactivity of the $[C_6H_6NO]^-$ adduct described later will show that NO addition to the ring of biradical negative ion **2** is the most likely outcome of reaction (2). Nitrogen dioxide, NO_2, reacts with both $C_6H_6^{\bullet -}$ and **7** exclusively by electron transfer forming NO_2^-. This is expected since the electron affinity of NO_2 (2.273 ± 0.005 eV)[37] is much greater than the electron binding energies of anions **2**, **4**, **5** and **6** (*vide infra*). Upon reaction of $C_6H_6^{\bullet -}$ with O_2 in either the flow tube or Q2, significant depletion of the reactant ion signal occurs, but no product ion signals are observed. This is interpreted as associative or reactive detachment, wherein the initial $[C_6H_6O_2]^{\bullet -}$ product or its prompt fragment ions are formed with sufficient excess internal energy to lose an electron prior to detection. Similar behavior has been reported for other distonic ions.[15b,27] Much slower signal depletion occurs when O_2 reacts with **7**, but again no product ions are observed in the mass spectrum. This behavior differs from that observed for the acyclic pentadienyl anion, $CH_2{=}CHCH{=}CHCH_2^-$, which undergoes oxidative cleavage with O_2 in the gas phase to form HO^-, $CH_2{=}CHO^-$ and $CH_2{=}CHCH{=}CHO^-$.[38] Dimethyl disulfide, CH_3SSCH_3, has been used to reveal reactive radical sites in distonic radical cations[39] and anions.[27] However, its non-radical reactivity with simple closed shell anions limits its usefulness for characterizing radical anions.[40] $C_6H_6^{\bullet -}$ reacts with dimethyl disulfide in the flow tube by thiomethyl abstraction to produce $[C_6H_6SCH_3]^-$ [eqn. (3a)], methanethiolate

$$C_6H_6^{\bullet -} + CH_3SSCH_3 \longrightarrow [C_6H_6SCH_3]^- + CH_3S \qquad (3a)$$

$$\longrightarrow CH_3S^- + (C_6H_7 + CH_2S) \text{ or } (C_6H_6SCH_3) \qquad (3b)$$

$$\longrightarrow C_6H_7 + C_2H_5S_2^- \qquad (3c)$$

formation [eqn. (3b)] and proton abstraction [eqn. (3c)] in 8, 10 and 82% yields, respectively.

The latter two ions are commonly formed in reactions of anions with dimethyl disulfide. The CH_3S^- product could arise by ($E_{CS}2$) elimination, in which case ($C_6H_7 + CH_2S$) are the neutral products, or by electron transfer from the nascent thiomethyl abstraction product to CH_3S radical within the ion–molecule complex, in which case ($C_6H_6SCH_3$) is the neutral product. The proton abstraction product, $C_2H_5S_2^-$, has been shown[40] to have the rearranged structure $CH_3SCH_2S^-$. Reaction of dimethyl disulfide with **7** produces CH_3S^- and $CH_3SCH_2S^-$ in 85 and 15% yields, respectively.

$C_6H_6^{\bullet -}$ and carbanion **7** were allowed to react with the electrophilic reagents CO_2, COS, and CS_2. Like most carbanions,[41] both ions undergo termolecular addition of CO_2 to yield the corresponding carboxylates [eqn. (4)].

$$C_6H_6^{\bullet -} + CO_2 \longrightarrow [C_6H_6CO_2]^{\bullet -} \qquad (4)$$

$C_6H_6^{\bullet -}$ reacts with both CS_2 and COS by sulfur atom abstraction and addition [*e.g.* eqn. (5)], but with opposite

$$C_6H_6^{\bullet -} + CS_2 \longrightarrow [C_6H_6S]^{\bullet -} + CS \qquad (5)$$
$$\longrightarrow [C_6H_6CS_2]^{\bullet -}$$

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‡ Reaction of $CH_2^{\bullet -}$ with NO to give $CH_2{=}NO^-$ is exothermic by approximately 95 kcal mol^{-1}.[45]

Table 2 Acid–base bracketing results for $C_6H_6^{\bullet -}$, $C_6H_7^-$ (**7**) and C_6H_8 (**3**)

$$\text{(i)}\ C_6H_6^{\bullet -} + HA \longrightarrow A^- + C_6H_7$$
$$\text{(ii)}\ C_6H_7^-\ (\mathbf{7}) + HA \longrightarrow A^- + C_6H_8$$
$$\text{(iii)}\ C_6H_8\ (\mathbf{3}) + A^- \longrightarrow HA + C_6H_7^-\ (\mathbf{7})$$

		Proton transfer observed?		
HA	ΔG_{acid}/kcal mol^{-1} [a]	eqn. (i)	eqn. (ii)	eqn. (iii)
D_2O	387.0 ± 0.2	No		
Pr^i_2NH	382.8 ± 0.4	No		
Furan	380.0 ± 3.0	No		
Cyclohexene	379.0 ± 5.0	No		
CH_2ClF	376.7 ± 0.3 [b]	Slow		
CH_3OH	375.1 ± 0.2 [c]	Yes		
$PhCH_3$	374.9 ± 0.2 [d]	Yes		
$H_2C{=}C{=}CH_2$	372.8 ± 3.0	Slow		
EtOH	372.0 ± 0.6 [c]	Yes		
Pr^iOH	370.1 ± 0.6 [c]	Yes		
HF	365.1 ± 0.3			Yes
$PhCH_2CH_2CH_2OH$	364.6 ± 0.8 [e]		No	Yes
$PhCH_2OH$	363.4 ± 2.0	Yes	No	Yes
PhCH(Me)OH	361.3 ± 0.5 [e]	Yes	Slow	Yes
CF_2HCH_2OH	359.2 ± 2.0	Yes	Yes	Yes
CH_3CHO	359.0 ± 2.0	Yes	Yes	Yes
$(CH_2F)_2CHOH$	356.7 ± 4.0		Yes	No
CF_3CH_2OH	354.1 ± 2.0	Yes	Yes	No
$CF_3C(CH_3)_2OH$	353.5 ± 2.0		Yes	No

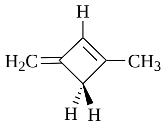
[a] Gas-phase acidities taken from reference 45 unless noted otherwise. [b] Reference 46. [c] K. M. Ervin, S. Gronert, S. E. Barlow, M. K. Gilles, A. G. Harrison, V. M.Bierbaum, C. H. Depuy, W. C. Lineberger and G. B. Ellison, *J. Am. Chem. Soc.*, 1990, **113**, 5750. [d] Reference 60. [e] Reference 47.

selectivity, *i.e.* 68% S-atom abstraction from CS_2; 28% from COS. Carbanion **7** reacts with CS_2 and COS exclusively by addition [*e.g.* eqn. (6)].

$$C_6H_7^- + CS_2 \longrightarrow C_6H_7CS_2^- \qquad (6)$$

Sulfur abstraction from CS_2 and COS is usually associated with strongly basic carbanions,[42] but this reaction can also be initiated by the radical site in distonic radical anions,[18,27,33] and it has recently been observed to occur to the neutral carbene moiety of a gaseous distonic carbene anion.[43]

Hydrogen–deuterium exchange and proton-transfer reactions are useful probes of carbanion structure.[44] Before describing these results, we must first consider the site of protonation of $C_6H_6^{\bullet -}$ and **7**, since the latter ion and the candidate structures for $C_6H_6^{\bullet -}$ are ambident species. The DFT calculations indicate that the methylmethylenecyclobutene isomer **8** is lower in enthalpy than dimethylenecyclobutane **3** by 3.8 kcal mol^{-1}. This means that the thermodynamic protonation site of carbanion **7** is one of the exocyclic methylene groups. In contrast, the linearly conjugated radical **9** is lower in energy than cross-conjugated radical **10** by 9.8 kcal mol^{-1}, so a thermodynamically controlled protonation of biradical negative ion **2** would occur on the ring. Thermodynamic protonation of isomers **4** and **6** occurs at their respective divalent carbons to give radical **9**.



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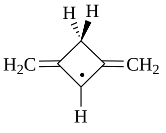

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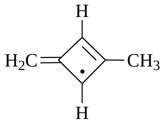

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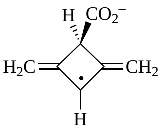
Neither $C_6H_6^{\bullet -}$ nor carbanion **7** displays any H/D exchange with D_2O, MeOD, EtOD, or Pr^iOD. However, D^+ transfer to $C_6H_6^{\bullet -}$ is observed to occur from EtOD and Pr^iOD, whereas carbanion **7** does not abstract D^+ from any of the deuteriated reagents. These observations indicate that $C_6H_6^{\bullet -}$ is a stronger base than EtO^-, and carbanion **7** is a weaker base than Pr^iO^- (neglecting the small differences in acidities between the deuteriated and undeuteriated acids). The absence of H/D exchange by $C_6H_6^{\bullet -}$ and **7** may be contrasted with the behavior of the acyclic pentadienyl anion [$\Delta H_{acid}(CH_2{=}CHCH{=}CHCH_3) = 369.2$ kcal mol^{-1}],[45] which slowly exchanges up to four hydrogens in the presence of MeOD.[44b]

The proton affinities of $C_6H_6^{\bullet -}$ and **7** and the gas-phase acidity of **3** were estimated by acid–base bracketing experiments. The occurrence or non-occurrence of proton transfer was monitored in reactions of the two anions with neutral compounds having known acidities, and in reactions between hydrocarbon **3** and anions with known proton affinities. Table 2 summarizes the results. Proton transfer to $C_6H_6^{\bullet -}$ occurs from CH_3OH [$\Delta G_{acid}(CH_3OH) = 375.1 \pm 0.2$ kcal mol^{-1}][45] and from each of the stronger acids examined, while no proton transfer occurs from CH_2ClF [$\Delta G_{acid}(CH_2ClF) = 376.7 \pm 0.3$ kcal mol^{-1}][46] or any of the weaker acids. Carbanion **7** slowly abstracts a proton from PhCH(Me)OH [ΔG_{acid}(PhCH(Me)OH) = 361.3 ± 0.5 kcal mol^{-1}],[47] CF_2HCH_2OH [$\Delta G_{acid}(CF_2HCH_2OH) = 359.2 \pm 2.0$ kcal mol^{-1}],[45] and from each of the stronger acids used, while no proton abstraction occurs from $PhCH_2OH$ [$\Delta G_{acid}(PhCH_2OH) = 363.4 \pm 2.0$ kcal mol^{-1}] or from any of the weaker acids that were examined. Proton abstraction from hydrocarbon **3** occurs with acetaldehyde enolate (CH_2CHO^-), $CF_2HCH_2O^-$, and with each of the stronger bases examined, while proton transfer does not occur to either $CF_3CH_2O^-$ or $CF_3C(CH_3)_2O^-$. Thus, a clear difference is observed between the apparent acidity of **3** and the apparent basicity of **7**. We interpret this as experimental confirmation of the theoretical prediction mentioned above that **7** preferentially protonates at an exocyclic methylene group to give the more stable tautomer **8** rather than **3**.

From the bracketing results we assign the acidity of the C_6H_7 radical formed by protonating $C_6H_6^{\bullet -}$ to be $\Delta G_{acid}(C_6H_7) = 376.0 \pm 2.0$ kcal mol^{-1}, and the ΔG_{acid} values for **3** and **8** are determined to be 358.5 ± 3.0 and 361.9 ± 2.0 kcal mol^{-1}, respectively. The corresponding enthalpy terms, $\Delta H_{acid}(C_6H_7)$, $\Delta H_{acid}(\mathbf{3})$ and $\Delta H_{acid}(\mathbf{8})$, can be calculated using the relation $\Delta H_{acid} = \Delta G_{acid} + T\Delta S_{acid}$, where ΔS_{acid} is the entropy change for acid dissociation given by $\Delta S_{acid}(HA) = S(H^+) + S(A^-) - S(HA)$.[48] The absolute entropy of a proton $S(H^+)$ is 26.0 eu,[49] and the difference in absolute entropies of A^- and HA can be estimated by the rotational contribution, $R\ln[\sigma(HA)/\sigma(A^-)]$, where σ is the rotational symmetry number. For hydrocarbon **3**

(D_{2h}, $\sigma = 4$) going to carbanion **7** (C_{2v}, $\sigma = 2$), ΔS_{acid} is equal to $S(H^+) + R\ln(2) = 27.3$ eu, while for hydrocarbon **8** (C_s, $\sigma = 1$), ΔS_{acid} is equal to $S(H^+) + R\ln(½) = 24.6$ eu. Assuming that $C_6H_6^{\cdot -}$is ion **2** (D_{2h}, $\sigma = 4$), ΔS_{acid} for C_6H_7 (C_{2v}, $\sigma = 2$) is also computed to be $26.0 + R\ln(½) = 24.6$ eu. Therefore, at 298 K $\Delta H_{acid}(C_6H_7) = 383.3 \pm 2.0$ kcal mol^{-1}, $\Delta H_{acid}(\mathbf{3}) = 366.7 \pm 3.0$ kcal mol^{-1} and $\Delta H_{acid}(\mathbf{8}) = 369.2 \pm 2.0$ kcal mol^{-1}. The 2.5 ± 3.6 kcal mol^{-1} difference in the acidities of **3** and **8** corresponds to the difference in enthalpy between these two tautomers, with **8** being more stable than **3**. The computed proton affinity of ion **2** derived from the B3LYP/6-31+G* calculations (*vide infra*) is 379 kcal mol^{-1}, while the proton affinities computed for isomers **4** and **6** are much higher, 390.2 and 392.4 kcal mol^{-1}, respectively. Thus, the acid–base bracketing results are more consistent with the formation of **2** as the product of reaction (1a).

The preliminary conclusion from the single-step ion–molecule reactions described above is that the $C_6H_6^{\cdot -}$ product of reaction (1a) is entirely the biradical negative ion **2**. This structure assignment is fully confirmed by the behavior of $C_6H_6^{\cdot -}$ in sequential ion–molecule reactions with two different neutral reagents. In order to properly interpret the outcome of a two-step reaction sequence, we must know the regiochemistry of the first step. Consider, for example, the addition of CO_2 to $C_6H_6^{\cdot -}$ to form a distonic carboxylate radical anion [eqn. (4)]. The calculations show that radical anion isomers **4** and **6** have $^2B_1$ and $^2A''$ ground states, respectively, with $\sigma^2\pi^5$ valence electron configurations (*i.e.* they are σ anion/π-radicals). Therefore, electrophilic addition of CO_2 to **4** and **6** necessarily occurs at the divalent carbons in each to yield distonic anions with the carboxylate moiety attached to the central- and terminal-positions of linearly conjugated pentadienyl radicals, respectively. For biradical negative ion **2**, carboxylation can in principle occur at either the ring or exocyclic methylene sites. By analogy with the strong preference for ring protonation of **2**, we assume a general preference for electrophilic addition to the ring site as well. Thus, carboxylation of **2** most likely produces distonic ion **11**.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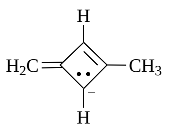
Similar conclusions are made for the preferred sites of radical attack on ions **2**, **4** and **6**. The DFT calculations indicate that the linearly conjugated carbanion **7** is lower in energy than cross-conjugated isomer **12** by 25.6 kcal mol^{-1}. Thus, H-atom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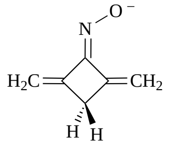
addition to **2**, **4** and **6** to form anion **7** is strongly preferred.§ We assume this regioselectivity holds for addition of other radical reagents as well.

Reaction of NO_2 with the $[C_6H_6CO_2]^{\cdot -}$ product of eqn. (4) yields an adduct as the sole ionic product. Coupling with NO_2 has been observed previously in our laboratory for distonic carboxylate ions derived from biradical and triradical negative ions.[13,33] However, we have found that α-distonic carboxylate radical anions such as $[CH_2CO_2]^{\cdot -}$[21] and $[PhCHCO_2]^{\cdot -}$[29] react exclusively by NO_2 addition accompanied by CO_2 loss to give the corresponding nitro anions [*e.g.* eqn. (7)]. The exclusive

$$[RCHCO_2]^{\cdot -} + NO_2 \longrightarrow RCHNO_2^- + CO_2 \quad (7)$$
$$R = Ph, H$$

formation of an adduct when $[C_6H_6CO_2]^{\cdot -}$ reacts with NO_2 is most consistent with structure **11** (and hence isomer **2** for $C_6H_6^{\cdot -}$), since NO_2 addition to the α-positions of the carboxylated forms of **4** or **6** should lead to some observable decarboxylation. However, this does not rule out a conceivable γ-addition to carboxylated **4** or γ- or ε-addition to carboxylated **6**.

The reactivity and apparent basicity of the NO adduct of $C_6H_6^{\cdot -}$ [eqn. (2)] are also indicative of structure **2**. Based on the expected regioselectivity for radical additions noted above, NO-addition to **4** and **6** should produce oximate anions **13** and **14**,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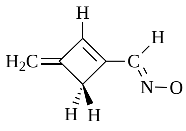
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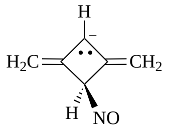
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respectively (provided associative detachment does not occur), while NO-addition to ion **2** would produce **15**—a species containing a linear pentadienyl carbanion moiety and a remote nitroso group. Recognizing that oximate anions are weaker bases than dienylic carbanions,[45] we attempted to identify the structure of the NO adduct of $C_6H_6^{\cdot -}$ from its acid–base behavior. The proton affinities of conjugated oximate anions such as **13** and **14** are estimated[45] to be about 355 kcal mol^{-1}, while the proton affinity of **15** should be slightly less than that of carbanion **7**, about 365 kcal mol^{-1}. Therefore, we evaluated the apparent basicity of the NO adduct of $C_6H_6^{\cdot -}$ by examining its proton transfer reaction with CF_3CH_2OH ($\Delta H_{acid} = 361.8$ kcal mol^{-1}[45]) in Q2 of the triple quadrupole analyzer, reasoning that if the adduct is **15**, exothermic proton transfer will occur, while if it is either **13** or **14**, proton transfer should be endothermic and will not occur at low collision energies. In fact, the former behavior was clearly evident: proton transfer from CF_3CH_2OH to $C_6H_6NO^-$ forming $CF_3CH_2O^-$ occurred at the lowest collision energies, with an energy-resolved reaction cross section that is typical of an exothermic process (Scheme 1). In keeping with the preferred site of protonation of carbanion **7**, Scheme 1 shows protonation of **15** at the exocyclic methylene group. Nevertheless, the conclusion is the same regardless of the site of protonation: exothermic proton abstraction from CF_3CH_2OH identifies $C_6H_6NO^-$ as structure **15** and, therefore, its $C_6H_6^{\cdot -}$ precursor as **2**. Furthermore, the working hypothesis for this experiment could be validated by demonstrating that addition of the stronger acid Pr^{i}SH ($\Delta H_{acid} = 353.4$ kcal mol^{-1}[45]) to the flow tube catalyzes the conversion of **15** to an oximate anion (either the structure shown in Scheme 1 or **13**), which effectively shuts down the proton abstraction from CF_3CH_2OH taking place at low collision energies in Q2.

The electron affinity of 2,4-dimethylenecyclobutane-1,3-diyl

Having established that the $C_6H_6^{\cdot -}$ product of reaction (1a) is pure biradical negative ion **2**, we next turned to a determination of its electron binding energy [or, equivalently, E_{ea} (**1**)] with use of the kinetic method.[50] Ion **2** reacts with SO_2 in the flow tube by termolecular association and by electron transfer [$E_{ea}(SO_2) = 1.107 \pm 0.008$ eV[51]] [eqn. (8)]. Collision-induced dissociation

$$C_6H_6^{\cdot -}\ (\mathbf{2}) + SO_2 \longrightarrow [C_6H_6SO_2]^{\cdot -} \quad (8)$$
$$\longrightarrow C_6H_6\ (\mathbf{1}) + SO_2^{\cdot -}$$

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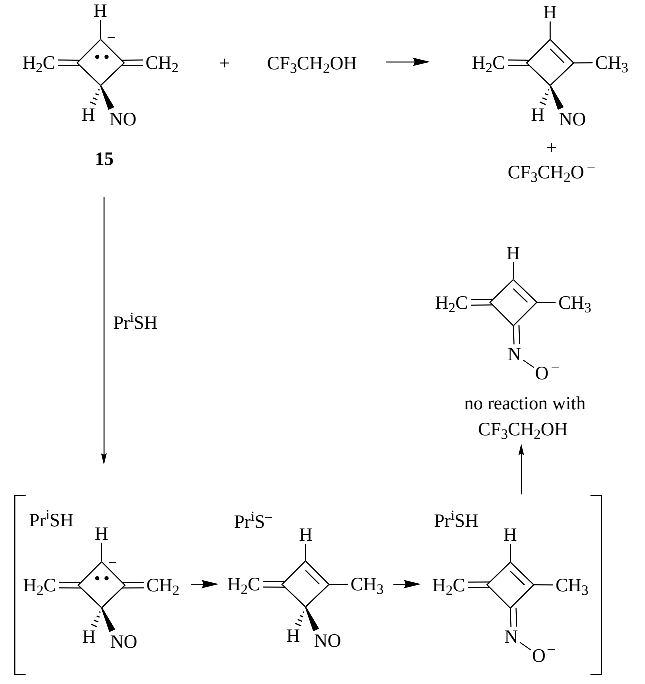
§ It should be noted that the thermodynamically preferred H-atom (or radical) addition to the divalent carbon atoms of **4** and **6** forming carbanion **7** necessarily involves a curve-crossing and, thus, may be associated with a barrier.

Table 3 Fragment ion yield ratios, $r = I(\mathrm{R}^-/\mathrm{SO_2}^{\bullet-})$, resulting from CID of $[\mathrm{R}^- + \mathrm{SO_2}]$ adducts, and the electron affinities of the reference neutral compounds, R

Compound (R)	E_{ea}(R)/eV	r[a]
3-Methylbenzyl radical	0.905 ± 0.006[b]	0.127 ± 0.010
Benzyl radical	0.912 ± 0.006[c]	0.098 ± 0.011
m-Xylylene biradical	0.919 ± 0.008[b]	0.153 ± 0.010
p-Fluorobenzyl radical	0.937 ± 0.008[d]	0.179 ± 0.010
Phenyl radical	1.096 ± 0.006[c]	2.21 ± 0.23
m-Fluorobenzyl radical	1.173 ± 0.008[d]	3.95 ± 0.10
p-Chlorobenzyl radical	1.174 ± 0.008[d]	3.60 ± 0.42
m-Chlorobenzyl radical	1.272 ± 0.008[d]	12.9 ± 1.0
m-Bromobenzyl radical	1.307 ± 0.008[d]	24.0 ± 0.8
2,4-Dimethylenecyclobutane-1,3-diyl biradical (**1**)	*1.14 ± 0.01*[e]	2.72 ± 0.15
2,4-Dimethylenecyclobutyl radical (**9**)	*1.14 ± 0.01*[e]	2.81 ± 0.11

[a] Uncertainties are one standard deviation from the average of replicate measurements. [b] Reference 53(*a*). [c] Reference 53(*b*). [d] Reference 53(*c*). [e] *This work.*



Scheme 1

of the adduct yields **2** and $\mathrm{SO_2}^{\bullet-}$ as the only ionic products. The apparent CID onsets are about 1.5 eV (center-of-mass frame; CM) for formation of **2**, and about 0.9 eV (CM) for formation of $\mathrm{SO_2}^{\bullet-}$. The fragment ion yield ratio, $r = I[\mathbf{2}]/I[\mathrm{SO_2}^{\bullet-}]$, resulting from CID of the adduct at 5 eV (CM) with 0.035 mTorr Ar target pressure is determined to be 2.72 ± 0.15, where the uncertainty reflects the precision of replicate measurements.

In recent studies of the benzyne anions[13b] and other carbanions,[52] we have shown that the measured $[\mathrm{R}^-]/[\mathrm{SO_2}^{\bullet-}]$ and $[\mathrm{R}^-]/[\mathrm{COS}^{\bullet-}]$ yield ratios obtained from CID of $\mathrm{SO_2}$ and COS adducts of the corresponding carbanions R^- display good semi-logarithmic relationships with known values of E_{ea}(R). These relationships can be used to determine an unknown electron binding energy for a carbanion from the measured yield ratio obtained from CID of its $\mathrm{SO_2}$- or COS-adduct. Accordingly, a calibration relation for the $I[\mathbf{2}]/I[\mathrm{SO_2}^{\bullet-}]$ ratio indicated above was constructed by measuring $[\mathrm{R}^-]/[\mathrm{SO_2}^{\bullet-}]$ ratios from CID of a series of $\mathrm{RSO_2}^-$ adducts for which values of E_{ea}(R) were known. The calibration series encompassed both even- and odd-electron reference anions for which accurate values of the electron affinities of the corresponding radicals and biradicals had been determined by negative ion photoelectron spectroscopy.[53] Table 3 lists the calibrants and their electron affinities, as well as the CID yield ratios obtained from replicate measurements. A plot of E_{ea}(R) *vs.* $\ln r = \ln(I[\mathrm{R}^-]/I[\mathrm{SO_2}^{\bullet-}])$ is presented in Fig. 1. A weighted linear least squares analysis of the data results in the following calibration relation with $r^2 = 0.992$ [eqn. (9)]. The electron affinity of **1** calculated with

$$E_{ea} = (24.58 \pm 0.13\ \mathrm{kcal\ mol^{-1}}) + (1.72 \pm 0.06\ \mathrm{kcal\ mol^{-1}})\ln r \qquad (9)$$

this equation from the measured CID ratio for its $\mathrm{SO_2}$ adduct is 26.3 ± 0.2 kcal mol^{-1} (1.14 ± 0.01 eV), where the assigned uncertainty is determined in the manner described previously.[21]

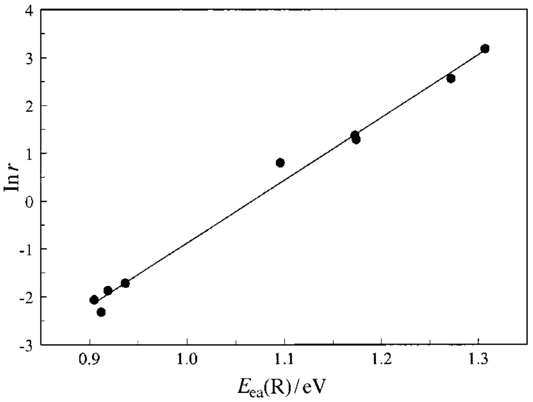


Fig. 1 Calibration plot for determination of the electron affinities of biradical **1** and monoradical **9** by the kinetic method. See Table 3 for specific values of E_{ea}(R) and *r*.

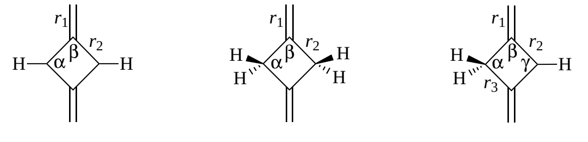
For comparison, the electron binding energy of carbanion **7** [or, equivalently, $E_{ea}(\mathbf{9})$] was determined by this same approach. Reaction of $\mathrm{SO_2}$ with **7** also proceeds by addition and electron transfer, and CID of the $\mathrm{C_6H_7SO_2}^-$ adduct yields only **7** and $\mathrm{SO_2}^{\bullet-}$. The measured yield ratio obtained from CID of the adduct under identical conditions as those used for the $\mathrm{SO_2}$ adduct of **2** is 2.81 ± 0.11. This value combines with calibration relation (9) to give $E_{ea}(\mathbf{9}) = 26.3 \pm 0.2$ kcal mol^{-1} (1.14 ± 0.01 eV). Thus, the measured electron affinities for biradical **1** and monoradical **9** are the same, *i.e.* introduction of the additional open-shell site in **9** to give **1** has no effect on the EA. For comparison, the measured electron affinity of trimethylenemethane, $E_{ea} = 9.96 \pm 0.14$ kcal mol^{-1}[54] (0.431 ± 0.006 eV), is 1.6 kcal mol^{-1} lower than that of 2-methylallyl radical, $E_{ea} = 11.6 \pm 0.14$ kcal mol^{-1}[55] (0.505 ± 0.006 eV). We also note that the measured EAs for **1** and **9** are between those of pentadienyl radical, $E_{ea} = 21.0 \pm 0.7$ kcal mol^{-1}[56] (0.91 ± 0.03 eV), and heptatrienyl radical, $E_{ea} = 29.3 \pm 0.7$ kcal mol^{-1}[56] (1.27 ± 0.03 eV).

Calculated structures and thermochemistry

Ab initio calculations of the structures and thermochemical properties of **1**, **2**, **3** and selected isomers were carried out to aid interpretation of the reactivity studies, and to provide theoretical models for the gas-phase acidity and electron affinity measurements. Density functional theory with a B3LYP/6-31+G* procedure was employed because of its good track record[57] for thermochemical calculations of this type, and its computational efficiency for molecules of this size.

Optimized geometries obtained at the B3LYP/6-31+G* level for **1**–**3**, **7** and **9** are summarized in Table 4. Calculated total energies, zero-point energies and thermal corrections for these species and related compounds are listed in Table 5, along with the calculated 298 K enthalpy differences between $\mathrm{C_6H_6}^{\bullet-}$, $\mathrm{C_6H_7}^-$ and $\mathrm{C_6H_8}$ isomers. Fig. 2 illustrates selected isomer enthalpy differences, along with the calculated values for the gas-phase CH acidities (ΔH_{acid}, 298 K) at different positions of each compound. The calculated electron affinities (E_{ea}, 0 K) for **1**, **9**, **10** and **16** are also indicated.

Table 4 Selected geometrical parameters for **1**–**3**, **7** and **9**[a]



1 and **2** **3** **7** and **9**

Structure	r_1	r_2	r_3	α	β	γ
1 D_{2h}	1.366	1.461		90.7	89.3	
2 D_{2h}	1.373	1.463		92.8	87.1	
3 D_{2h}	1.331	1.531		87.8	96.2	
7 C_{2v}	1.371	1.427	1.542	86.0	89.5	94.9
9 C_{2v}	1.359	1.429	1.541	85.0	90.7	93.5

[a] Bond distances in Å; angles in degrees.

Table 5 B3LYP/6-31+G* electronic energies, zero-point energies, 298 K temperature corrections, and relative 298 K enthalpies for C_6H_n (n = 6,7,8) ions and neutral molecules[a]

Compound,[b] point group (state)	E_{elec}	ZPE[c]	$H_{298} - H_0$[c]	$H_{\text{rel,298}}$
C_6H_6				
1 $D_{2h}(^3B_{2u})$	−232.105 87	56.0	4.2	(0)
16 $C_{2v}(^3B_1)$	−232.073 04	57.2	4.0	21.6
Benzene $D_{6h}(^1A_1)$	−232.258 93	61.3	3.2	−91.8
$C_6H_6^{\bullet-}$				
2 $D_{2h}(^2B_{3g})$	−232.143 39	54.6	4.5	(0)
4 $C_{2v}(^2B_1)$	−232.121 82	55.6	4.2	14.3
5 $C_{2v}(^2B_2)$	−232.092 80	56.2	4.2	33.1
6 $C_s(^2A'')$	−232.116 52	54.7	4.0	16.4
C_6H_7				
9 $C_{2v}(^2B_1)$	−232.757 01	64.6	4.1	(0)
10 $C_s(^2A'')$	−232.741 19	64.0	4.6	9.8
$C_6H_7^-$				
7 $C_{2v}(^1A_1)$	−232.795 17	63.3	4.3	(0)
12 $C_1(^1A)$	−232.753 84	62.6	4.6	25.6
C_6H_8				
3 $C_{2v}(^1A_1)$	−233.386 49	72.5	4.3	(0)
8 $C_s(^1A')$	−233.393 03	72.7	4.4	−3.8

[a] Total energies in atomic units; all other quantities in kcal mol^{-1}. [b] See the text and Fig. 2 for compound structures. [c] Computed vibrational frequencies scaled by a factor of 0.972.

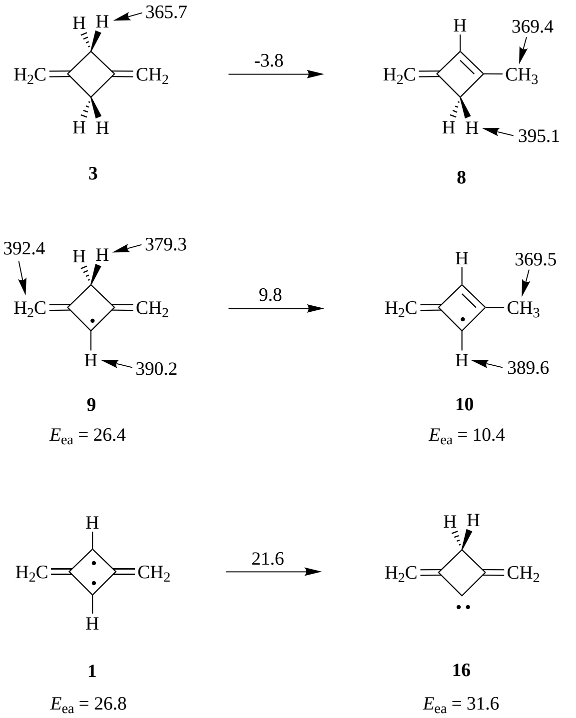
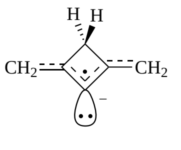


Fig. 2 Thermochemical properties (in kcal mol^{-1}) of selected C_6H_n (n = 6,7,8) species obtained from B3LYP/6-31+G* calculations. Values of ΔH_{acid} (298 K) shown for indicated CH bonds.



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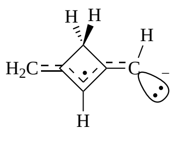

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The optimized geometry derived from DFT calculations for the (D_{2h}) $^3B_{2u}$ ground state of biradical **1** is essentially identical with that obtained by Borden and co-workers from a π-CISD approach.[9a] The singlet states of **1** were not examined in the present work. The near-degenerate pair of non-bonding π MOs of **1** containing the two valence electrons are of b_{1u} and b_{3g} symmetry. Thus, formation of the biradical negative ion **2** by addition of a third electron produces a $^2B_{3g}$ state [$(b_{1u})^2(b_{3g})^1$ occupation] and a $^2B_{1u}$ state [$(b_{1u})^1(b_{3g})^2$ occupation]. Like the singlet ^1A_g state of **1**, the radical anion doublet states of **2** are subject to Jahn–Teller distortion from D_{2h} to C_{2v} symmetry *via* a b_{2u} mode.[9] At the B3LYP/6-31+G* level of theory, the calculated potential surface for this distortion is sufficiently flat that geometry optimization for **2** leads to a D_{2h} structure with an electron configuration corresponding to the $^2B_{3g}$ state. The lack of Jahn–Teller distortion by **2** is reminiscent of our earlier findings for the benzyne anions: DFT calculations (B3LYP/cc-pVDZ) also showed no tendency to distort the high-symmetry, delocalized states of these radical anions [$D_{2h}(^2A_g)$ for *p*-benzyne anion; $C_{2v}(^2B_2)$ for *o*- and *m*-benzyne anions] to lower symmetry, localized radical anion forms.[25] The optimized structure for **2** is only slightly perturbed from that of **1**, *i.e.* less than 0.007 Å increases in the bond distances and 2° changes in the ring bond angles. Similar geometry changes are evident in going from monoradical **9** to anion **7**—small increases of the CC bonds, and small, compensatory changes in the ring bond angles such that the dienylic carbanion moiety becomes slightly elongated. A D_{2h} structure with distinct bond length alternation is found for **3**.

The calculations predict biradical negative ion **2** to be the lowest energy $C_6H_6^{\bullet-}$ isomer (Table 5) by at least 14 kcal mol^{-1}. The odd spin density and negative charge density in **2** are delocalized over the entire six-atom π-system, while isomers **4** and **6** are (σ,π) radical anions in which either spin or charge must be formally localized at the divalent carbon in each. As indicated earlier, the DFT calculations lead to $^2B_1$ and $^2A''$ ground states for **4** and **6**, respectively, with $\sigma^2\pi^5$ valence electron configurations corresponding to deprotonated pentadienyl radicals (**4** and **6**). Similar preferences for σ-anion/π-radical states are found in calculations on $PhCH^{\bullet-}$[29] and α,3-dehydrotoluene radical anion.[58]

Biradical **1** is calculated to be 92 kcal mol^{-1} higher in energy than benzene, locating it well above all closed-shell C_6H_6 isomers in energy,[45] but 22 kcal mol^{-1} lower in energy than the dimethylenecyclobutylidene isomer **16** (also a ground-state triplet). The enthalpy difference between hydrocarbon tautomers **3** and **8** (−3.8 kcal mol^{-1}) can be understood in terms of π-conjugation and strain effects, while the inverted stability orderings for radicals **9** and **10** (9.8 kcal mol^{-1}), and for anions **7** and **12** (25.6 kcal mol^{-1}) arise from both strain and electronic destabilization of the π systems in **10** and **12**.[59]

The different gas-phase CH acidities illustrated in Fig. 2 were all calculated with use of an isodesmic reaction approach, *i.e.* by computing the acidities relative to a reference compound with a similar type of CH bond, and then deriving the absolute acidity from the experimental value for the reference compound. The acidities of the allylic CH positions in **3**, **8**, **9** and **10** were calculated relative to propene ($\Delta H_{\text{acid}} = 391.1 \pm 0.3$ kcal mol^{-1}[60]), *e.g.* eqn. (10), while the vinyl CH acidities of **9** and **10**

$$\mathbf{2} + CH_2{=}CHCH_3 \longrightarrow \mathbf{9} + CH_2CHCH_2^- \qquad (10)$$

were calculated relative to methyl radical ($\Delta H_{\text{acid}} = 408.6 \pm 0.6$ kcal mol^{-1}[45]), *e.g.* eqn. (11).

$$\mathbf{4} + CH_3 \longrightarrow \mathbf{9} + CH_2^{\bullet -} \qquad (11)$$

Similarly, the theoretical predictions for the electron affinities shown in Fig. 2 were derived by computing electron affinities relative to a reference radical, biradical or carbene, and then combining this with the experimental EA for the reference species. For biradical **1**, the electron affinity was calculated relative to trimethylenemethane, $E_{\text{ea}}(\text{TMM}) = 9.96 \pm 0.14$ kcal mol^{-1}[54] [eqn. (12)]. For all the monoradicals including **9** the

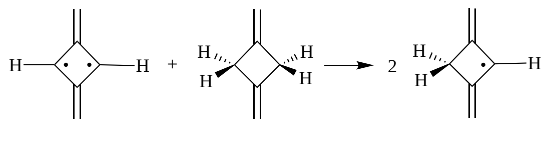
$$\mathbf{2} + \text{TMM} \longrightarrow \mathbf{1} + [\text{TMM}]^{\bullet -} \qquad (12)$$

electron affinities were computed relative to the allyl radical, $E_{\text{ea}}(CH_2CHCH_2) = 11.1 \pm 0.18$ kcal mol^{-1}[55] [*e.g.* eqn. (13)].

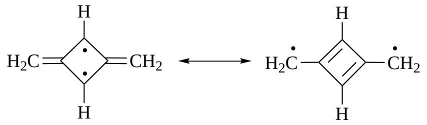
$$\mathbf{7} + CH_2CHCH_2 \longrightarrow \mathbf{9} + CH_2CHCH_2^- \qquad (13)$$

For carbene **16** the electron affinity was calculated relative to methylene, $E_{\text{ea}}(CH_2) = 15.0 \pm 0.14$ kcal mol^{-1}.[11] The electron affinities of **1** and **9** derived from B3LYP/6-31+G* calculations, 26.8 and 26.4 kcal mol^{-1}, respectively, are in excellent agreement with the measured values, and provide theoretical support for the conclusion that the EAs of the mono- and bi-radical are the same.

The experimental value for $\Delta H_{\text{acid}}(C_6H_7)$, 383.3 ± 2.0 kcal mol^{-1}, is in fair agreement with the acidity predicted for the allylic CH position of radical **9**, 379.3 kcal mol^{-1}, but differs significantly from the acidities predicted for the allylic position of **10**, or any of the vinyl CH positions in both radicals (Fig. 2). This supports the $C_6H_6^{\bullet -}$ ion structure assignment and the conclusion that radical ion **2** protonates on the ring to give **9**. The experimentally determined acidity of **3**, 366.7 ± 3.0 kcal mol^{-1}, is in good agreement with the theoretically predicted value, 365.7 kcal mol^{-1}, as is the **3**→**8** enthalpy difference (2.5 *vs.* 3.8 kcal mol^{-1}). Experiment and theory concur that hydrocarbon **3** is a stronger acid than monoradical **9** by 14–17 kcal mol^{-1}. Radical and biradicals can be either stronger[21,13] or weaker[54] acids than the corresponding even-electron species, depending upon the particulars of the valence orbital topology. The difference in the gas-phase acidities **3** and **9** is much larger than the difference in the experimentally determined acidities of 2-methylallyl radical (394 ± 2 kcal mol^{-1}[54]) and 2-methylpropene (390.3 ± 2.3 kcal mol^{-1}[45]). A useful perspective can be obtained by dissecting the acidities of **3** and **9** into the corresponding bond energy and electron affinity terms according to $\Delta H_{\text{acid}}(\text{RH}) = D(\text{RH}) - E_{\text{ea}}(\text{R}) + E_{\text{i}}(\text{H})$.[48] Since the electron affinities of **1** and **9** are measured and calculated to be identical (*cf.* Table 3 and Fig. 2), the large difference in the gas-phase acidities of **3** and **9** must be entirely due to a large difference in their CH bond energies. From the experimental acidities, electron affinities and the above relation we compute that reaction (14) is


(14)

exothermic by 16.6 ± 3.6 kcal mol^{-1}. This is supported by the DFT calculations, which give $\Delta H(14) = -13.2$ kcal mol^{-1}. Thus, the ‘first’ ring CH bond energy in 1,3-dimethylenecyclobutane **3** is much smaller than the ‘second’. This dramatic deviation from bond strength additivity for a system that gives a ground state triplet biradical is quite unusual,[61] and it indicates that **1** is significantly destabilized relative to two separate monoradicals. The origin of the effect is of course the dimethylenecyclobutadiene character of biradical **1**, which renders it partially antiaromatic.



Conclusions

The 2,4-dimethylenecyclobutane-1,3-diyl anion **2** has been generated in pure form in the gas phase from the reaction of atomic oxygen anion with 1,3-dimethylenecyclobutane **3**. The observed reactivity of this ion is consistent with the structural assignment, but different from that expected for possible carbene anion isomers. Several differences in the reactivities of **2** and the corresponding even-electron carbanion **7** are noted that are ascribed to radical-mediated processes by the former. These include coupling with NO, S-atom abstraction from CS_2 and COS, and CH_3S group abstraction from dimethyl disulfide. Acid–base bracketing experiments reveal that hydrocarbon **3** is a stronger acid than the radical 2,4-dimethylenecyclobutyl (**9**) by nearly 17 kcal mol^{-1}. In contrast, the electron affinities of biradical **1** and monoradical **9** determined by the kinetic method are found to be identical. These two facts, which are fully supported by *ab initio* calculations, require that the allylic ring CH bond strength in the monoradical 2,4-dimethylenecyclobutyl is nearly 17 kcal mol^{-1} greater than the ring CH bond strength in 1,3-dimethylenecyclobutane. This dramatic deviation from bond energy additivity in a system that produces a ground-state triplet biradical arises from antiaromatic destabilization of the π system in the biradical.

The synthesis and structure proof for ion **2** are a necessary prelude to its examination by negative ion photoelectron spectroscopy. Such studies can provide accurate measures of the electron affinity and singlet–triplet splitting of biradical **1**, as well as valuable information about the geometries and vibrational structures of both the ion and neutral species. The long history of fascination with ‘non-Kekulé benzene’, and current interests in this biradical in the context of organic ferromagnetism make it a compelling target for characterization by the photoelectron spectroscopy technique.

Acknowledgements

This work was supported by a grant from the National Science Foundation.

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Paper 7/07470K
Rceived 16*th October* 1997
Accepted 26*th November* 1997