Towards Stable Distonic Radical Anions: a Theoretical Study

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Ab initio molecular orbital calculations have been carried out to obtain the structures and relative isomer energies of organometallic radical anions of the types $CH_3X^{-\bullet}$ and $H_2C^{\bullet}-XH^-$ (X = Li, BeH, BH_2, Na, MgH, or AlH_2). Comparison with results for the corresponding neutral molecules indicates a dramatic reduction in the energy gap between classical and hydrogen-shifted isomers on addition of an electron. However, the classical isomers of the radical anions generally represent the preferred form. The only exception is $H_2C^{\bullet}-BH_3^-$, which is calculated to be virtually isoenergetic with $H_3CBH_2^{-\bullet}$. Organoborane radical anions are thus the most likely systems to adopt distonic structures with the formal charge and radical centres on different atoms. Further separation of the charge and the radical sites through homologation is predicted to be ineffective in stabilising the distonic structures. MNDO calculations on larger models point to experimentally accessible distonic radical anions. The present study leads to a better understanding of the origin of distonic stabilisation in radical ions.

Several simple organic radical cations prefer structures which differ dramatically from those of their neutral counterparts. For example, the radical cation of methanol is calculated to be 10.8 kcal mol^{-1} less stable than the isomeric $H_2C^{\bullet}-OH_2^+$.[1] In contrast, the ylide $H_2C^--OH_2^+$ is at best a shallow minimum on the potential energy surface[2] and is 89—93 kcal mol^{-1} higher in energy than H_3COH.[3,4] Hydrogen-shifted structures like $H_2C^{\bullet}-OH_2^+$, variously termed distonic radical cations (since the formal positive charge and the radical are localised on distal atoms),[5] ylide ions (as they are derived by ionisation of ylides),† and dipole-stabilised carbenes,[6] have attracted considerable attention in recent years. On the basis of systematic *ab initio* calculations, Radom and his co-workers have predicted numerous such unusual distonic radical cation structures to be more stable than corresponding classical isomers.[1,5] Several distonic radical cations have been observed experimentally by Schwarz,[6,7] McLafferty,[8] and Terlouw and others,[9] often by innovative design and occasionally as by-products of gas-phase fragmentation reactions. Many structures have now been unambiguously characterised.

In this paper, a computational search for analogous distonic radical anions is initiated. Specifically, we seek molecules for which hydrogen-shifted structures become energetically favourable by (and only by) the addition of an electron.

An understanding of the factors determining the relative stabilities of distonic radical cations is a useful starting point for designing stable distonic radical anions. The unusual energy difference between $H_2C^{\bullet}-OH_2^+$ and $CH_3OH^{+\bullet}$ probably reflects the destabilisation of the latter ion as a result of removal of an electron from an orbital localised on a highly electronegative atom. By similar reasoning, a classical isomer with a negative charge concentrated on an electropositive atom may be destabilised. Alternative structures in which the charge is dispersed over additional atoms may become favourable. This situation may be encountered in monomeric organometallic molecules of formula CH_3X (X = Li, BeH, BH_2, Na, MgH, or AlH_2), which have LUMOs virtually localised on an electropositive atom. The corresponding radical anions may therefore energetically prefer distonic structures of the form $H_2C^{\bullet}-XH^-$. We have computed the energy differences between classical and distonic forms for the foregoing series of radical anions using *ab initio* molecular orbital theory. Parallel calculations have been carried out on the corresponding neutral isomers to quantify the effect of an added electron on the relative stabilities of classical and ylide-like structures.

Our approach is first to establish general structural preferences in these mostly hypothetical systems by using an adequate theoretical model. After identification of the system most favouring a distonic structure, additional strategies are explored to obtain promising systems potentially accessible to experiment.

Computation

Ab initio calculations were performed by using the Gaussian 80 series of programs, modified for the DEC-10 computer.[10] All open-shell systems were examined at the Unrestricted Hartree-Fock (UHF) level.[11] Full geometry optimisation using analytical gradients[12] was carried out for all the systems considered with the split-valence 3-21G basis set.[13] For anionic systems, additional calculations with the 3-21+G basis set,[14] which includes a set of diffuse functions on all non-hydrogen atoms, were performed. Calculations at the 6-13G(*d*) level,[15] including a set of *d*-type polarisation functions on the heavy atoms, were also carried out for the boron derivatives.

Additional MNDO calculations[16] were performed on systems containing lithium, beryllium, boron, and aluminium. A few larger organoborane radical anions were also examined at the MNDO level. The half-electron (HE) method[17,18] was employed for describing open-shell systems in these semiempirical calculations.

Results and Discussion

The calculated total energies and relative isomer energies of $CH_3-X^{-\bullet}$ and $H_2C^{\bullet}-XH^-$ are presented in Table 1. The corresponding data for the neutral isomers at the 3-21G level are also shown for comparison.

For all the neutral molecules studied, the classical forms are preferred over ylide isomers, $H_2C^+-XH^-$, by 60—90 kcal mol^{-1}. In fact, many of the ylides could be examined only by imposing suitable symmetry constraints inhibiting hydrogen migration. An added electron has a substantial effect on the isomer energies, as seen from the ΔE_1 values [for reaction (1)] in Table 1.

$$H_3C-X^{-\bullet} \longrightarrow H_2C^{\bullet}-XH^- \qquad (1)$$

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† Ylide ions form a subclass of distonic radical cations, with the charge and radical sites located on adjacent atoms.

Table 1. Calculated total energies (Hartrees)[a] and relative isomer energies (kcal mol^{-1})[b]

		3-21G		3-21+G	
Molecule/Ion	Point group	$-E$	Rel. E	$-E$	Rel. E
$CH_3Li^{-\bullet}$	C_{3v}	46.747 96	0.0	46.766 60	0.0
$H_2C^{\bullet}$-LiH^-	C_{2v}	46.693 12	34.4	46.706 75	37.6
$CH_3BeH^{-\bullet}$	C_s	54.450 06	0.0	54.479 45	0.0
$H_2C^{\bullet}$-BeH_2^-	C_{2v}	54.446 08	2.5	54.461 57	11.2
$CH_3BH_2^{-\bullet}$	C_s	65.012 98	0.0	65.036 87	0.0
$H_2C^{\bullet}$-BH_3^-	C_s	65.016 31	−2.1	65.032 76	2.6
$CH_3Na^{-\bullet}$	C_{3v}	200.199 52	0.0	200.218 76	0.0
$H_2C^{\bullet}$-NaH^-	C_{2v}	200.128 68	44.5	200.146 77	45.2
$CH_3MgH^{-\bullet}$	C_s	238.387 40	0.0	238.407 83	0.0
$H_2C^{\bullet}$-MgH_2^-	C_{2v}	238.355 86	19.8	238.370 75	23.3
$CH_3AlH_2^{-\bullet}$	C_s	281.105 91	0.0	281.123 66	0.0
$H_2C^{\bullet}$-AlH_3^-	C_s	281.087 59	11.5	281.104 49	12.0
CH_3Li	C_{3v}	46.752 48	0.0		
CH_2LiH	C_{2v}	46.624 81	80.1		
CH_3BeH	C_{3v}	54.515 28	0.0		
CH_2BeH_2	C_{2v}	54.381 21	84.1		
CH_3BH_2	C_s	65.078 09	0.0		
CH_2BH_3	C_s	64.973 17	65.8		
CH_3Na	C_{3v}	200.200 30	0.0		
CH_2NaH	C_{2v}	200.065 39	84.7		
CH_3MgH	C_{3v}	238.413 62	0.0		
CH_2MgH_2	C_{2v}	238.276 50	86.0		
CH_3AlH_2	C_s	281.126 55	0.0		
CH_2AlH_3	C_s	280.994 82	82.7		

[a] From geometries obtained at the 3-21G level. [b] 1 kcal = 4.184 kJ.

The magnitude of the effect can be expressed by the energy of the isogyric reaction (2) (ΔE_2).* The ΔE_2 values shown in Table 2 are uniformly large and negative. The effect of the added electron is the least for Li and Na derivatives, for which the energy gap between the classical and ylide forms is reduced by 'only' *ca.* 40 kcal mol^{-1}. The change is much greater for radical anions containing Mg, B, Al, and Be, being of the order of 60—80 kcal mol^{-1}.

$$CH_2\text{-}XH + CH_3X^{-\bullet} \longrightarrow CH_2{}^{\bullet}\text{-}XH^- + CH_3\text{-}X \quad (2)$$

Although the energetic effect of an added electron is very large, the distonic form is not the favoured isomer in any of the cases considered. In particular, the isomers $H_2C^{\bullet}$-LiH^- and $H_2C^{\bullet}$-NaH^- are forbiddingly high in energy. Of the remaining systems, $H_2C^{\bullet}$-MgH_2^- is about 23 kcal mol^{-1} less stable than the classical isomer H_3C-$MgH^{-\bullet}$. The energy gap is just 11—12 kcal mol^{-1} for the Be and Al derivatives at the 3-21+G level. Clearly, the most favoured distonic radical anion is $H_2C^{\bullet}$-BH_3^-, which is calculated to be virtually isoenergetic with the classical isomer CH_3-$BH_2^{-\bullet}$. In fact, additional 6-13G(*d*) calculations predict the distonic isomer to be more stable by 5 kcal mol^{-1}.

The intrinsic preferences of various organometallic radical anions to adopt distonic structures obtained here refer only to hypothetical model systems in the gas phase. Two approaches are available for designing experimentally accessible systems which may favour distonic structures. One way is to increase the separation between the formally charged atom and the radicaloid carbon by introducing CH_2 groups. This strategy has been found quite effective in preferentially stabilising distonic radical cations.[5] For example, the energy separation favouring $H_2C^{\bullet}$-$[CH_2]_n$-OH_2^+ relative to H_3C-$[CH_2]_n$-$OH^{+\bullet}$ increases as *n* goes from 0 to 1, but reaches a constant value beyond $n = 3$.[5] Another approach is to use substituents to stabilise selectively distonic radical anions. The two methods are considered in turn.

Effect of Homologation.—A quick computational way to evaluate the energetic effect of increasing the separation between the radical and charge centres is by means of reaction (3).[5] In this isogyric reaction a negative charge and a radical centre localised on an electropositive group are separated in such a way that the charge ends up on a hyperco-ordinated atom X, while the radical is on carbon. The structural changes accompanying reaction (1) are similar. The only difference is that the charge and the radical centres are moved to adjacent atoms in (1), whereas they are infinitely separated in (3). However, the calculated energies ΔE_1 (Table 1) and ΔE_3 (Table 3) are not substantially different. In every system studied the two sets of numbers are within a few kcal mol^{-1} of each other. This implies that increasing the distance between the formal charge and the radical centre beyond $H_2C^{\bullet}$-XH^- does not lead to additional stabilisation of the distonic form. This conclusion may be quantified by using reaction (4). As seen from Table 4, the ΔE_4 values are generally small and, interestingly, positive. The corresponding values for stable distonic radical cations are negative.[5] Thus, short-range interactions between the charge and the radical are mildly stabilising for distonic radical anions, in contrast to the destabilisation found for radical cations. The net result is that distonic radical anions cannot be preferentially stabilised by simple homologation.

$$CH_3\text{-}X^{-\bullet} + H_3C\text{-}CH_3 \longrightarrow H_3C\text{-}XH^- + CH_3\text{-}CH_2{}^{\bullet} \quad (3)$$

$$H_2C^{\bullet}\text{-}XH^- + H_3C\text{-}CH_3 \longrightarrow H_3C\text{-}XH^- + H_3C\text{-}CH_2{}^{\bullet} \quad (4)$$

MNDO calculations on organoborane radical anions confirm the foregoing prediction. The calculated heats of formation of $H_2C^{\bullet}$-$[CH_2]_n$-BH_3^- and H_3C-$[CH_2]_n$-$BH_2^{-\bullet}$ are given in Table 5. The MNDO method overestimates the distonic stabilisation in the parent system [MNDO −21.6 *vs.* 6-31G(*d*) −5.0 kcal mol^{-1}]. However, the key result is the virtual constancy of the classical–distonic energy difference for *n* = 0, 1, or 2. The consistency of the MNDO and *ab initio* results suggests that homologation will not be effective in preferentially stabilising distonic forms in any of the radical anion systems considered here.

Substituent Effects.—A promising approach to alteration of the relative stabilities of distonic and classical radical anions is by means of selective substitution. The classical isomers would be stabilised by both donor and acceptor groups at the electropositive atom. On the other hand, distonic forms would be more sensitive to substituent effect at the radicaloid carbon. MNDO calculations on substituted organoborane radical anions (Table 5) are illustrative. Both donors and acceptors at boron stabilise the classical isomer $BR_3^{-\bullet}$, just as they stabilise isoelectronic $CR_3^{\bullet}$.[19] The distonic forms gain little from substitution at boron. Therefore, substantially reduced energies are obtained for the reactions (5)—(7) relative to the un-

$$H_3C\text{-}B(H)(CH_3)^{-\bullet} \longrightarrow H_2C^{\bullet}\text{-}B(H)_2(CH_3)^- \quad (5)$$
$$-17.6 \text{ kcal mol}^{-1}$$

$$H_3C\text{-}B(H)(CN)^{-\bullet} \longrightarrow H_2C^{\bullet}\text{-}B(H)_2(CN)^- \quad (6)$$
$$-15.8 \text{ kcal mol}^{-1}$$

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* Reactions in which the spin multiplicities are conserved are isogyric reactions.

Table 2. Calculated energies (kcal mol^{-1}) of reaction (2)

Reaction	MNDO	3-21G	3-21+G[a]
$CH_2LiH + [CH_3Li]^{-\bullet} \longrightarrow [CH_2LiH]^{-\bullet} + CH_3Li$	−79.2	−45.7	−42.5
$CH_2BeH_2 + [CH_3BeH]^{-\bullet} \longrightarrow [CH_2BeH_2]^{-\bullet} + CH_3BeH$	−85.5	−81.6	−72.9
$CH_2BH_3 + [CH_3BH_2]^{-\bullet} \longrightarrow [CH_2BH_3]^{-\bullet} + CH_3BH_2$	−58.2	−67.9	−63.2
$CH_2NaH + [CH_3Na]^{-\bullet} \longrightarrow [CH_2NaH]^{-\bullet} + CH_3Na$		−40.2	−39.5
$CH_2MgH_2 + [CH_3MgH]^{-\bullet} \longrightarrow [CH_2MgH_2]^{-\bullet} + CH_3MgH$		−66.2	−62.7
$CH_2AlH_3 + [CH_3AlH_2]^{-\bullet} \longrightarrow [CH_2AlH_3]^{-\bullet} + CH_3AlH_2$	−62.8	−71.2	−70.7

[a] Energies obtained at the 3-21G level used for the neutral species.

Table 3. Calculated energies (kcal mol^{-1}) of reaction (3)

Reaction	3-21G	3-21 + G[a]
$[CH_3Li]^{-\bullet} + C_2H_6 \longrightarrow [CH_3LiH]^- + CH_3CH_2^\bullet$	41.8	45.9
$[CH_3BeH]^{-\bullet} + C_2H_6 \longrightarrow [CH_3BeH_2]^- + CH_3CH_2^\bullet$	10.0	19.6
$[CH_3BH_2]^{-\bullet} + C_2H_6 \longrightarrow [CH_3BH_3]^- + CH_3CH_2^\bullet$	1.1	7.8
$[CH_3Na]^{-\bullet} + C_2H_6 \longrightarrow [CH_3NaH]^- + CH_3CH_2^\bullet$	51.0	53.3
$[CH_3MgH]^{-\bullet} + C_2H_6 \longrightarrow [CH_3MgH_2]^- + CH_3CH_2^\bullet$	26.2	31.1
$[CH_3AlH_2]^{-\bullet} + C_2H_6 \longrightarrow [CH_3AlH_3]^- + CH_3CH_2^\bullet$	14.8	16.7

[a] Energies obtained at the 3-21G level used for the neutral species.

Table 4. Calculated energies (kcal mol^{-1}) of reaction (4)

Reaction	MNDO	3-21G	3-21+G[a]
$[CH_2LiH]^{-\bullet} + C_2H_6 \longrightarrow [CH_3LiH]^- + CH_3CH_2^\bullet$	−0.8	7.4	8.3
$[CH_2BeH_2]^{-\bullet} + C_2H_6 \longrightarrow [CH_3BeH_2]^- + CH_3CH_2^\bullet$	1.9	7.5	8.4
$[CH_2BH_3]^{-\bullet} + C_2H_6 \longrightarrow [CH_3BH_3]^- + CH_3CH_2^\bullet$	0.0	3.2	5.2
$[CH_2NaH]^{-\bullet} + C_2H_6 \longrightarrow [CH_3NaH]^- + CH_3CH_2^\bullet$		6.5	8.1
$[CH_2MgH_2]^{-\bullet} + C_2H_6 \longrightarrow [CH_3MgH_2]^- + CH_3CH_2^\bullet$		6.4	7.8
$[CH_2AlH_3]^{-\bullet} + C_2H_6 \longrightarrow [CH_3AlH_3]^- + CH_3CH_2^\bullet$	−0.2	3.3	4.7

[a] Energies obtained at the 3-21G level used for the neutral species.

Table 5. MNDO heats of formation (kcal mol^{-1}) of organoborane radical anions

Radical ion	ΔH_f°	Radical ion	ΔH_f°
$CH_3BH_2^{-\bullet}$	1.3	$CH_2^\bullet$–BH_3^-	−20.3
$CH_3CH_2BH_2^{-\bullet}$	−4.9	$CH_3CH^\bullet$–BH_3^-	−32.3
$CH_2^\bullet$–$CH_2BH_3^-$	−26.5	$(CH_3)_2BH^{-\bullet}$	−17.1
$CH_2^\bullet$–$BH_2CH_3^{-\bullet}$	−34.7	n-$C_3H_7BH_2^{-\bullet}$	−9.9
$C_2H_5CH^\bullet$–BH_3^-	−37.4	$CH_3CH^\bullet$–$CH_2BH_3^-$	−37.4
$CH_2^\bullet$–$CH_2CH_2BH_3^-$	−31.2	$CH_2^\bullet$–$BH(CH_3)_2^-$	−46.1
$(CH_3)_3B^{-\bullet}$	−32.2	$(CH_3)_2CHBH_2^{-\bullet}$	−4.6
$(CH_3)_2C^\bullet$–BH_3^-	−41.1	$(CN)CH_2BH_2^{-\bullet}$	20.9
$(CN)CH^\bullet$–BH_3^-	−7.9	$(CH_3)(CN)HB^{-\bullet}$	−7.0
$CH_2^\bullet$–$BH_2(CN)^-$	−22.8		

$$H_3C\text{–}B(CH_3)_2^{-\bullet} \longrightarrow H_2C^\bullet\text{–}B(H)(CH_3)_2^- \quad (7)$$
$$-13.9 \text{ kcal mol}^{-1}$$

substituted system (−21.6 kcal mol^{-1}). On the other hand, a donor or an acceptor substituent at the radicaloid carbon alters the energies in favour of distonic forms [reactions (8)—(11)].

$$H_3C\text{–}CH_2\text{–}BH_2^{-\bullet} \longrightarrow H_3C\text{–}CH^\bullet\text{–}BH_3^- \quad (8)$$
$$-27.4 \text{ kcal mol}^{-1}$$

$$C_2H_5\text{–}CH_2\text{–}BH_2^{-\bullet} \longrightarrow C_2H_5\text{–}CH^\bullet\text{–}BH_3^- \quad (9)$$
$$-27.5 \text{ kcal mol}^{-1}$$

$$n\text{-}C_3H_7\text{–}BH_2^{-\bullet} \longrightarrow CH_3\text{–}CH^\bullet\text{–}CH_2\text{–}BH_3^- \quad (10)$$
$$-27.5 \text{ kcal mol}^{-1}$$

$$NC\text{–}CH_2\text{–}BH_2^{-\bullet} \longrightarrow NC\text{–}CH^\bullet\text{–}BH_3^- \quad (11)$$
$$-28.8 \text{ kcal mol}^{-1}$$

Obviously, a better way of preferentially stabilising the distonic isomer is by having two substituents at the radicaloid carbon [reaction (12)].

$$(H)(CH_3)_2C\text{–}BH_2^{-\bullet} \longrightarrow (CH_3)_2C^\bullet\text{–}BH_3^- \quad (12)$$
$$-36.5 \text{ kcal mol}^{-1}$$

The foregoing conclusions must hold good for the radical anions containing other electropositive elements as well. In all the cases, the radical carbon of the distonic form provides a convenient handle for substituent stabilisation. Since this is a common feature in all the distonic isomers, the magnitude of substituent effects should also be similar. It should therefore be possible to modify the stability order in favour of distonic forms even for radical anions containing beryllium and aluminium.

Prospects for Experimental Observation.—Relatively little is known of organometallic radical anions experimentally. By a happy coincidence, many of the available results relate to organoborane radical anions, which are indicated by the preceding calculations to be the most likely system to prefer distonic structures. Stabilised borane radical anions like $BH_2CN^{-\bullet}$ have been characterised by e.s.r. spectroscopy.[20] Even an *X*-ray crystal structure has been recently determined for a triarylborane radical anion.[21] While these ions have no distonic alternatives, the foregoing studies at least prove that long-lived organoborane radical anions can be made in condensed phases. A promising approach is therefore to make organoborane radical anions containing radical-stabilising substituents at a carbon atom adjacent to boron. Both donors and acceptors would be effective. A combination of donor and acceptor substituents which takes advantage of the symbiotic captodative stabilisation of a radical[22] should prove even more effective. Since salts of the kind $Na^+ BR_3^{-\cdot}$ have long been known,[23] suitable alkyl or benzyl groups can be chosen to favour distonic structures. For example, isopropylborane radical anion would be a good candidate, on the basis of MNDO calculations.

In the foregoing analysis, thermodynamic stability alone has been considered. But this does not ensure the formation of distonic forms. The important question concerning the barrier to hydrogen shift from carbon to boron needs to be examined. The rearrangement involves a cyclic three-centre, three-electron bond in the transition state. On a qualitative basis, this entails a large barrier. Similar electronic structures are also involved in the transition states separating classical and distonic radical cations. Available calculations indicate the presence of barriers of the order of 20—35 kcal mol^{-1} (for F, O systems)[1a,5c,24] or 45—50 kcal mol^{-1} (for S, P systems).[5c,25] Rearrangement leading to the formation of distonic radical anions should involve similar barriers. Inter- rather than intra-molecular processes may therefore be necessary for successful experimental observation of distonic radical anions.

The present calculations refer to isolated gas-phase species. Substantial changes in energetics may arise from solvation and counterion effects. One can only speculate about these factors. Polar media and counterions like Na^+ should preferentially stabilise classical isomers since the negative charge is more localised in these structures. Counterions with a more diffuse charge like tetra-alkylammonium ion may be more appropriate to stabilise distonic radical anions.

The speculations in this section derive strong support from recent studies on isoelectronic boron-containing radicals.[26–28] Reaction of borane–amine adducts with t-butoxyl radical leads to the initial formation of $R_2HN\text{–}BH_2^{\cdot}$, which rearranges to $R_2N^{\cdot}\text{–}BH_3$.[26] Remarkably, the hydrogen migration has been determined by means of isotopic labelling to be an intermolecular rather than an intramolecular process. *Ab initio* calculations also reveal the greater stability of the latter nitrogen-centred radical. Similar results have also been obtained for analogous phosphine adducts.[27] Since the more stable radical is isoelectronic with distonic $H_2C^{\cdot}\text{–}BH_3^-$ and the less stable isomer corresponds to the classical methyl-borane radical anion, the foregoing observations entirely parallel the conclusions from the present work.

Origin of Distonic Stabilisation in Radical Ions.—How is it that numerous radical cations containing electronegative atoms prefer distonic structures,[5] while the majority of radical anions with electropositive groups are reluctant to do likewise? Two factors appear important in determining the relative energies of classical and distonic forms. In the case of $CH_3\text{–}BH_2^{-\cdot}$ and $H_2C^{\cdot}\text{–}BH_3^-$, the classical isomer has a localised negative charge at boron making it disfavoured. In the distonic structure only the formal charge is on boron, with the real charge distributed over its neighbours. This is generally true of all hyperco-ordinated 'ate' anions, such as $R\text{–}Li\text{–}R^-$, R_3Be^-, and R_4B^-. The redistribution of charge away from the electropositive atom favours the distonic isomer relative to the classical form. However, a second factor has an opposing effect. In simple Lewis terms, the carbon has an octet of electrons while the boron has only a septet in $CH_3\text{–}BH_2^{-\cdot}$. The situation is reversed in the distonic isomer with the carbon having only a septet of electrons. Thus, electron deficiency is passed on to carbon in the distonic form. However, the more electronegative carbon would clearly prefer to have its full complement of eight electrons. As a result, the distonic isomer is relatively destabilised. These two opposing factors, *viz.* preference of an electropositive atom for reduced negative charge by formation of an 'ate' structure and preference of the more electronegative carbon for an octet of electrons, lead to the calculated relative energies in Table 1. Only in the case of organoborane radical anions does the former factor dominate sufficiently to yield thermodynamically more stable distonic structures.

Interestingly, in radical cations such as $CH_3OH^{+\cdot}$ and $H_2C^{\cdot}\text{–}OH_2^+$, the charge redistribution effect and the octet preference reinforce each other. Since the HOMO of methanol is essentially a nonbonding orbital on oxygen,[29] the positive charge in $CH_3\text{–}OH^{+\cdot}$ is virtually localised on the more electronegative atom. In the distonic form, the positive charge on the 'onium' ion is distributed over the neighbours of oxygen. Furthermore, the more electronegative atom has its formal share of eight electrons only in the distonic structure. Both effects clearly favour the distonic isomer. The relative energies in radical cations should therefore be simply related to the electronegativity differences. The *ab initio* results of Radom and his co-workers on a variety of systems are entirely consistent with this view.[5] Thus, the most favourable distonic radical cations obtained by them were $H_2C^{\cdot}\text{–}OH_2^+$ and $H_2C^{\cdot}\text{–}FH^+$.

In summary, electronegativity differences play a key role in determining the relative stability of classical and distonic radical cations. The electronegativity effect is less clear-cut with radical anions. The structural preference in these latter systems is a balance of two opposing effects, both determined by relative electronegativities.

Conclusions

Ab initio calculations on radical anions containing electropositive groups indicate that distonic isomers, which have their formal charge and radical centres on different atoms, are generally less stable than classical forms. The only clear exception is $H_2C^{\cdot}\text{–}BH_3^-$, which is calculated to be more or less equal in energy to $H_3C\text{–}BH_2^{-\cdot}$. While homologation is ineffective in preferentially stabilising distonic structures, selective use of substituents appears promising. Suitable systems for experimental observation are radical anions of organoboranes, which have radical-stabilising substituents at an α-carbon atom.

The present study provides useful insights into the factors influencing the stability of radical ions in general. Additional calculations on other potentially distonic radical ions based on these ideas are under way.

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