Semi-empirical MNDO-SCF Study of the Molecular and Electronic Structures of Some Permethylated σ^* Radicals

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Molecular and electronic structures have been calculated, using the MNDO method, for a range of permethylated σ^* radicals, of general constitution $\mathrm{Me}_n\mathrm{M}\dot{-}\mathrm{M'Me}_{n'}$. When M = M′, radicals based upon second-row M are all calculated to be genuine σ^* radicals, but when M is a first-row element, all the systems studied except for $\mathrm{Me}_6\mathrm{C}_2^-$ are calculated to be very weak complexes of $\mathrm{Me}_n\mathrm{M}\colon$ and $\mathrm{Me}_n^{\bullet}$ having long M $\cdots$ M distances; $\mathrm{Me}_6\mathrm{C}_2^-$ is calculated to dissociate completely to $\mathrm{Me}_3\mathrm{C}^-$ and $\mathrm{Me}_3\mathrm{C}^{\bullet}$. When M $\neq$ M′ and M is a first-row element and M′ is a second-row element, genuine σ^* radicals are formed only when M and M′ are together of low electronegativity: high electronegativity of M and M′ leads either to weak complexes of $\mathrm{Me}_n\mathrm{M}\colon$ + $\mathrm{Me}_{n'}\mathrm{M}'^{\bullet}$ or to complete dissociation.

Electron-loss from non-metal alkyls such as $\mathrm{Me_2S}$ or $\mathrm{Me_3P}$ can yield not only the corresponding cation radicals, but also the dinuclear radicals $\mathrm{Me_4S_2}^+$ or $\mathrm{Me_6P_2}^+$.[1,2] These species are σ^* radicals in which the unpaired electron is largely confined to an anti-bonding orbital between the two heavy atoms. Electron loss from the first-row analogue $\mathrm{Me_2O}$ yields both the parent cation radical and also radicals arising from hydrogen-atom transfer processes,[3,4] but no dinuclear radical $\mathrm{Me_4O_2}^+$ has been detected. In fact, very few σ^* radicals of type $\mathrm{X}_n\mathrm{M}\dot{-}\mathrm{M'X'}_{n'}$ are known in which both of M,M′ are first row elements: the sole examples appear to be $\mathrm{F_2}^-$, the anion $\mathrm{N_2O_4}^-$ derived from $\mathrm{N_2O_4}$,[5] and a series of radical anions derived from oxoanions, $(\mathrm{ClO_4})_2^-$, $(\mathrm{BrO_4})_2^-$, and $(\mathrm{WO_4})_2^{3-}$, and the radical cation $[(\mathrm{HO})_5\mathrm{IO}]_2^+$ derived from periodic acid.[6]

In a semi-empirical SCF-MO study of the radical cations derived from simple ethers, it was found[7] that for $\mathrm{Me_4O_2}^+$ there was in fact a weakly exothermic complex of $\mathrm{Me_2O}$ and $\mathrm{Me_2O}^+$ having a long oxygen–oxygen distance of 3.44 Å; the calculated spin-density distribution for this complex was such that, based upon hyperfine couplings alone, the complex would be experimentally indistinguishable from isolated $\mathrm{Me_2O}^+$.

The general question of the stability of σ^* radicals containing first-row M,M′ has been raised[6,8] and we have consequently undertaken a semi-empirical study of a range of permethylated σ^* radicals, using the MNDO method.[9–11] We have sought to establish both geometric and electronic structures of the genuine σ^* radicals, and to distinguish between the case of formation of weakly exothermic complexes and of no complex formation at all where genuine σ^* radicals are absent.

Calculations

All calculations were performed using the MNDO method[9,10] implemented on a VAX 11/780 computer, with UHF wavefunctions for all open-shell species, and the published parameterisation.[9–11] Except where stated to the contrary, all geometric variables were independently optimised without constraints: in the exploration of the potential minima in the first-row systems $\mathrm{Me}_n\mathrm{M}\dot{-}\mathrm{MMe}_n$, the geometry was optimised for each radical at a series of fixed values of the M-M distance. Difficulties in convergence were experienced for the two mixed M,M′ radicals $\mathrm{Me_3SiFMe}$ and $\mathrm{Me_3NClMe}^+$: no conclusions can therefore be drawn for these species.

Results and Discussion

The radicals to be considered all have the general form $\mathrm{Me}_n\mathrm{M}\dot{-}\mathrm{M'Me}_{n'}$. It is convenient firstly to consider in turn those in which M,M′ are identical second-row atoms, then those where M,M′ are identical first-row atoms, and finally mixed species.

M,M′ *both Second-row Atoms.*—Free optimisation of the geometries of $\mathrm{Me_6Si_2}^-$, $\mathrm{Me_6P_2}^+$, $\mathrm{Me_4P_2}^-$, $\mathrm{Me_4S_2}^+$, $\mathrm{Me_2S_2}^-$, and $\mathrm{Me_2Cl_2}^+$ yielded the parameters given in Table 1. In all cases the two 'halves' of each radical optimised to identical geometries, with identical electron distributions. This, and the symmetric nature of the SOMO (A_{2u} in D_{3d}; B_u in C_{2h}; and B in C_2) demonstrates that these radical ions are all genuine σ^* radicals. For n = 2 or 3, it is noteworthy that the angle $(\mathrm{C}\widehat{\mathrm{M}}\mathrm{C})$ is

Table 1. Optimised molecular parameters for second-row σ^* radicals $\mathrm{Me}_n\mathrm{M}\dot{-}\mathrm{MMe}_n$

Radical	Point-group	ΔH_f°/kJ mol^{-1}	d(CM)/Å	d(MM)/Å	$(\mathrm{C}\widehat{\mathrm{M}}\mathrm{C})/^{\circ}$ [a]	$(\mathrm{C}\widehat{\mathrm{M}}\mathrm{M})/^{\circ}$	δ(CMMC)/°	$\Delta(\Delta H_f^{\circ})$/kJ mol^{-1} [b,c]
$\mathrm{Me_6Si_2}^-$	D_{3h}	−722.3	1.863	2.369	104.6	114.0	60.0	−177.0
$\mathrm{Me_6P_2}^+$	D_{3h}	+286.1	1.783	2.174	108.1	110.8	60.0	−176.1
$\mathrm{Me_4P_2}^-$	C_{2h}	−410.3	1.741	2.129	106.6	109.0	67.6	−147.7
$\mathrm{Me_4S_2}^+$	C_{2h}	+679.4	1.768	2.191	106.4	108.8	64.4	−114.7
$\mathrm{Me_2S_2}^-$	C_2	−189.1	1.704	2.074		112.9	100.0	−152.1
$\mathrm{Me_2Cl_2}^+$	C_{2h}	+804.0	1.879	2.238		108.4	180.0	−164.7

[a] Calculated values of $(\mathrm{C}\widehat{\mathrm{M}}\mathrm{C})$ in $\mathrm{Me_3Si}^{\bullet}$, $\mathrm{Me_3P}^+$, $\mathrm{Me_2P}^{\bullet}$, and $\mathrm{Me_2S}^+$ are 113.5, 118.1, 108.1, and 109.4°, respectively. [b] ΔH° for association reaction; $\mathrm{Me}_n\mathrm{M}\colon + \mathrm{Me}_n\mathrm{M}^{\bullet} \longrightarrow \mathrm{Me}_n\mathrm{M}\dot{-}\mathrm{MMe}_n$. [c] Calculated ΔH_f°/kJ mol^{-1} for fragments $\mathrm{Me}_n\mathrm{M}\colon$ are: $\mathrm{Me_3Si}^-$, −363.2; $\mathrm{Me_3P}$, −201.8; $\mathrm{Me_2P}^-$, −209.9; $\mathrm{Me_2S}$, −71.3; MeS^-, −123.9; MeCl, −92.3; for fragments $\mathrm{Me}_n\mathrm{M}^{\bullet}$, calculated values are: $\mathrm{Me_3Si}^{\bullet}$, −182.1; $\mathrm{Me_3P}^+$, +664.0; $\mathrm{Me_2P}^{\bullet}$, − 52.7; $\mathrm{Me_2S}^+$, +865.4; $\mathrm{MeS}^{\bullet}$, +86.9; MeCl^+, +1 061.0.

Table 2. Calculated spin density and observed hydrogen hyperfine couplings for second-row radicals, $Me_nM\dot{-}MMe_n$ and $Me_nM^\bullet$

	$Me_nM\dot{-}MMe_n$		$Me_nM^\bullet$	
Me_nM	$\rho(^1H)^a$	$A(^1H)/G$	$\rho(^1H)^a$	$A(^1H)/G$
Me_3Si	$-0.0046(\times 18)$		$-0.0014(\times 9)$	6.3^e
Me_3P	$0.0016(\times 18)$	3.3^b	$0.0158(\times 9)$	11.5^f
Me_2P	$0.0054(\times 12)$		$0.0187(\times 6)$	
Me_2S	$0.0051(\times 12)$	6.3^c	$0.0212(\times 6)$	20.5^g
MeS	$0.0070(\times 6)$	5.0^d	$0.0230(\times 3)$	
MeCl	$0.0047(\times 6)$		$0.0315(\times 3)$	

[a] Calculated values of $\rho[M(3s)]$ are: $Me_6Si_2^-$, 0.234; $Me_6P_2^+$, 0.137; $Me_4P_2^-$, 0.094; $Me_4S_2^+$, 0.027; $Me_2S_2^-$, 0.036; $Me_2Cl_2^+$, 0.004; $Me_3Si^\bullet$, 0.205; Me_3P^+, 0.077; $Me_2P^\bullet$, 0.022; Me_2S^+, 0.010; $MeS^\bullet$, 0.006; $MeCl^+$, 0.001. [b] $A(^{31}P)$, 503 G (ref. 1). [c] Ref. 2. [d] T. Gillbro, *Chem. Phys.*, 1974, **4**, 476. [e] $A(^{29}Si)$, 191 G (ref. 14). [f] $A(^{31}P)$, 385 G (ref. 1). [g] Ref. 13.

Table 3. Results for first-row radicals $Me_nM\dot{-}MMe_n$

Radical	$\Delta H_f^\ominus$/kJ mol^{-1}	d(M–M)/Å	$\Delta(\Delta H_f^\ominus)$/kJ mol^{-1}
$Me_6C_2^-$	*a*	*a*	*a*
$Me_6N_2^+$	+777.4	4.09	−13.8
$Me_4N_2^-$	+122.4	4.60	−19.3
$Me_4O_2^+$	+543.0	3.44	−23.8
$Me_2O_2^-$	−210.1	4.74	−19.3
$Me_2F_2^+$	+643.7	3.72	−32.5

[a] No minimum detected: $Me_6C_2^-$ dissociates to $Me_3C^\bullet$ and Me_3C^-.

always smaller in the dimer $Me_nM\dot{-}MMe_n$ than in monomeric $Me_nM^\bullet$, significantly so if $n = 3$, but only modestly so when $n = 2$.

The calculated values of $\Delta H_f^\ominus$ for the dimeric σ^* radical ($Me_nM\dot{-}MMe_n$), together with those of their component fragments $Me_nM\colon$ and Me_nM' (Table 1) show that for the association reaction [equation (1)] the $\Delta H_f^\ominus$ value is always large and negative where M is a second-row element, indicative of a fairly strong M–M bond in the σ^* radical. For comparison, the calculated values of the comparable dissociation energies $D(Me_nM{-}MMe_n)$ for the neutral closed-shell species Me_6Si_2, Me_4P_2, and Me_2S_2 are 173.4, 200.0, and 250.3 kJ mol^{-1} respectively.

$$Me_nM\colon + Me_nM^\bullet \longrightarrow Me_nM\dot{-}MMe_n \qquad (1)$$

Table 2 records the calculated values of the spin density at hydrogen in both $Me_nM\dot{-}MMe_n$ and $Me_nM^\bullet$, together with the observed $A(^1H)$ values, where these are known. It is clear that in all cases there is a substantial difference in the calculated values of $\rho(^1H)$ for the dimeric and monomeric radicals; this is consistent with the marked decrease in the observed value of $A(^1H)$ upon dimerisation. A similar decrease occurs upon dimer formation of $Me_4Se_2^+$ (A 4.9 G[12]) from Me_2Se^+ (A 15.6 G[13]). In contrast to this change, formation of analogous σ radicals from monomeric species effects little change in $A(^1H)$. Thus for the series of $Me_6M_2^+$ and $Me_3M^\bullet$ radicals the values of A are, respectively: M = Si, 5.6 G[14] and 6.4 G[15]; M = Ge, 5.3 G[16] and 5.3 G[17]; M = Sn, 3.4 G[18] and 2.8 G.[19] These findings together support our earlier view[20] that the changes in $A(^1H)$ upon dimer formation are dominated by the character, σ or σ^*, of the SOMO, rather than by changes[1] in the geometry of the heavy atom. We note here also that the calculated bond angles ($C\hat{M}C$) differ very little for the dimer and monomers $Me_4M_2^\pm$ and $Me_2M^\bullet$ (Table 1), again consistent with the view[20] that changes in central-atom geometry have minimal effects upon A in these radicals. We have noted elsewhere[21] the problem of establishing, within the MNDO parameterisation, an appropriate scale-factor related to the calculated values of spin density, ρ, and the observed hyperfine couplings, A.

M,M′ both First-row Atoms.—When M = M′, the pattern of behaviour is quite different from that found for second-row σ^* radicals; the salient results are listed in Table 3. For $Me_6C_2^-$, no minimum whatever was detected, and the calculations show that this radical dissociates completely to yield $Me_3C^\bullet$ and Me_3C^-: it should be emphasized that this result refers to the isolated gas-phase radical, and that the radical may survive in solid matrices,[20] in the same way as $Me_6C_2^+$.[14,22] For each of the other radicals in Table 3, a broad, shallow energy minimum was detected corresponding to a long M ··· M distance, and a rather low $\Delta H_f^\ominus$ for the association reaction [equation (1)]. In each case the two 'halves' of the radical were quite different: the geometry and electronic structure of one fragment was virtually identical to that of $Me_nM\colon$, and the other fragment was essentially unperturbed $Me_nM^\bullet$. In particular, the spin densities calculated for the $Me_nM^\bullet$ fragments in these complexes are virtually identical with the values calculated for isolated $Me_nM^\bullet$, so that the complexes will not be detectable on the basis of hyperfine couplings.

There are several factors which may contribute to the gross difference in behaviour of systems having both heavy atoms as either first- or second-row atoms. First, in neutral Me_6C_2, Me_4N_2, and Me_2O_2 the calculated bond dissociation energies $D(Me_nM{-}MMe_n)$ are all <75 kJ mol^{-1}, whereas for the second-row analogues these energies are all >175 kJ mol^{-1}; hence addition of an extra antibonding electron might be expected to be more likely to cause dissociation in the first-row series than in the second-row series. Secondly, the LUMO in each of the neutral $(Me_nM)_2$ species has strong σ^* character in the M–M interaction, and it is weakly bound when M = Si, P, or S, but unbound when M = C, N, or O; the HOMO–LUMO gap is correspondingly larger in the first-row species. Hence, it is entirely reasonable that electron attachment to neutral first-row $(Me_nM)_2$ species should cause a substantial increase in the M–M distance, but that for second-row species the M–M distances should be virtually unchanged. The polarity of the M–C–H fragment does not appear to be crucial. In neutral $(Me_nM)_2$, the M–C bond is polarised $M^{\delta-}{-}C^{\delta+}$ for M = C, N, O, and S; in Me_6Si_2 the polarisation is $Si^{\delta+}{-}C^{\delta-}{-}H^{\delta+}$ and in Me_4P_2, $P^{\delta-}{-}C^{\delta-}{-}H^{\delta+}$.

There remains the apparent anomaly of F_2^-. Experimental gas-phase date[23-26] indicate that both reactions [equation (2)] for X = F or Cl are exothermic by *ca.* 120 kJ mol$^-$. Both F_2^- and Cl_2^- are calculated to be symmetric σ^* radicals.

$$X^\bullet_{(g)} + X^-_{(g)} \longrightarrow X_2^-{}_{(g)} \qquad (2)$$

Mixed M,M′ Radicals.—The first category of radicals, having one each of M and M′ an atom of the first and second rows, which was considered was that having the same overall stoicheiometry $Me_nM\dot{-}M'Me_n$ as those considered above. Of these $Me_2OSMe_2^+$ and $MeFClMe^+$ were calculated to be weak complexes of Me_nM and $Me_{n'}M'$ (Table 4) in the manner of the first-row dimers, but the remainder were all calculated to be genuine σ^* radicals: in each case the calculated hydrogen spin-density was the more positive in the 'half' containing the more electronegative M. The SOMO was calculated to be concentrated in the M–M′ interaction, but in each case to be more concentrated on the less electronegative of M and M′: the principal contributions were from the *np* orbitals of both atoms, except for $Me_3CSiMe_3^-$ where the principal contribution of silicon is the 3*s* orbital.

Two further series of mixed M,M′ radicals were then in-

Table 4. Optimised molecular properties for mixed radicals $Me_nM\dot{-}M'Me_{n'}$

Radical	ΔH_f°/kJ mol^{-1}	d(M–M′)/Å	$\Delta(\Delta H_f^{\circ})$/kJ mol^{-1}	$\rho(CH_3\text{–}M)^a$	$\rho(CH_3\text{–}M')^a$	Comment
(a) Radicals of type $Me_nM\dot{-}M'Me_{n'}$						
$Me_3CSiMe_3^-$	−449.6	2.006	−42.6	0.0047	−0.0110	σ^*
$Me_3NPMe_3^+$	+559.5	1.993	−40.3	0.0043	0.0009	σ^*
$Me_2NPMe_2^-$	−158.5	1.830	−53.3	0.0053	0.0031	σ^*
$Me_2OSMe_2^+$	+633.0	3.62	−18.1	$\simeq 0$	0.0212	$\simeq(Me_2O + Me_2S^+)$
$MeOSMe^-$	−162.2	1.872	−14.0	0.0161	0.0082	σ^*
$MeFClMe^+$	+776.7	3.27	−29.4	$\simeq 0$	0.0288	$\simeq(MeF + MeCl^+)$
(b) Radicals of type $Me_3Si\dot{-}M'Me_{n'}$						
$Me_3SiCMe_3^-$	−449.6	2.006	−42.6	−0.0110	0.0047	σ^*
Me_3SiNMe_3	−241.7	2.040	−49.2	−0.0060	0.0007	σ^*
$Me_3SiNMe_2^-$	−414.4	1.870	−176.1	−0.0141	0.0011	σ^*
Me_3SiOMe_2	−439.5	1.952	−43.1	−0.0068	$\simeq 0$	σ^*
Me_3SiOMe^-	−640.3	1.774	−252.8	−0.0181	0.0018	σ^*
Me_3SiFMe	b					
(c) Radicals of type $MeCl\dot{-}M'Me_{n'}$						
$MeClCMe_3$	Dissociates to MeCl and $Me_3C^{\bullet}$					
$MeClNMe_3^+$	b					
$MeClNMe_2$	Dissociates to MeCl and $Me_2N^{\bullet}$					
$MeClOMe_2^+$	+660.7	3.59	−28.1	$\simeq 0$	0.0491	$\simeq(MeCl + Me_2O^+)$
$MeClOMe$	Dissociates to MeCl and $MeO^{\bullet}$					
$MeClFMe^+$	+776.7	3.27	−29.4	0.0288	$\simeq 0$	$\simeq(MeF + MeCl^+)$
(d) Miscellaneous radicals from electron attachment to stable neutral molecules						
$Me_3CPMe_2^-$	−221.6	2.056	−32.1	0.0104	0.0017	σ^*
Me_3CSMe^-	Dissociates to $Me_3C^{\bullet}$ and MeS^-					
Me_2POMe^-	−361.8	1.699	−127.6	−0.0037	0.0080	σ^*
Me_2NSMe^-	Dissociates to $Me_2N^{\bullet}$ and MeS^-					

[a] M,M′ identified as in column 1. [b] Failed to converge.

vestigated containing respectively the least and most electronegative of the second-row elements M. In the series $Me_3Si\dot{-}M'Me_{n'}$ containing the Me_3Si fragment, all species (Table 4) were found to be genuine σ^* radicals, except for Me_3SiFMe where no SCF convergence was achieved. On the other hand, of radicals $MeCl\dot{-}M'Me_{n'}$, containing the highly electronegative MeCl fragment, three ($MeClCMe_3$, $MeClNMe_2$, and MeClOMe) were calculated to dissociate completely, and two others ($MeClOMe_2^+$ and $MeClFMe^+$) gave minima corresponding to very weak complex formation: no genuine σ^* radicals were found in this series.

These three groups of mixed M,M′ radicals point strongly to the electronegativity of M and M′ as an important determinant of the formation and stability of σ^* radicals of type $Me_nM\dot{-}M'Me_{n'}$. When the electronegativity sum for M and M′ is too high the σ^* radical dissociates, either to the weak complex, or sometimes completely. These latter may of course form weak associations in frozen matrices, due to the operation of cage effects, as occurs in the σ radicals $Me_3C\text{–}CH_3^+$ and $Me_3C\text{–}CMe_3^+$. The contrasting results for $Me_2OSMe_2^+$ (weak complex) and $MeOSMe^-$ (σ^* radical) and for $MeFClMe^+$ (weak complex) and FCl^- (σ^* radical) indicate that, in the permethyl compounds at least, the degree of alkylation of a given central atom pair M,M′ is also important; more methyl groups for a given total electron count lead to a less stable σ^* radical, as the effective electronegativity sum for M and M′ is increased on methylation, by notional addition of CH_3^+ ions.

Consistent with this view, it is found that in the present isoelectronic series, the approximate upper limit for the sum of Pauling electronegativities of M and M′ which is consistent with the existence of a stable σ^* radical is 5.2 for hexamethyl species, 5.3 for tetramethyls, and 6.3 for dimethyls.

Finally, four additional species were considered which are potentially accessible by electron attachment to stable neutral molecules (Table 4). Of these, $Me_3CPMe_2^-$ and Me_2POMe^- are calculated to be stable σ^* radicals, while Me_3CSMe^- and Me_2NSMe^- are both calculated to undergo complete dissociation, in isolation. Overall these findings are broadly consistent with the above conclusions on the electronegativity of M and M′, and suggest that, for trimethyl species, the σ^* radicals are stable for a Pauling electronegativity sum of up to at least 5.6.

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