Semi-empirical SCF–MO Study of the Molecular and Electronic Structures of the Cation-radicals derived from Simple Ethers and Acetals

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Molecular and electronic structures have been calculated, using the MNDO method, for the cation-radicals derived from a number of simple ethers and acetals, both cyclic and acyclic. For Me_2O^+ and Et_2O^+ both inter- and intra-molecular hydrogen atom transfers, from carbon to oxygen, are exothermic processes. The cation-radical of 1,3-dioxolane is calculated to be planar, but those from 1,3-dioxane and 1,3,5-trioxane contain planar COCOC fragments with the sixth ring atom displaced from this plane; the calculated spin-densities in these two cations allow an assignment of the observed e.s.r. spectra to be made. No definitive distinction could be made between the boat and chair conformers of the 1,4-dioxane cation-radical.

Recent experimental interest[1-4] in the cation-radicals of simple ethers and acetals has focused on several points: the magnitude of the proton hyperfine coupling; the possibility of the formation of dimers $R_4O_2^+$, analogous to $R_4S_2^+$;[5] and the possibility of spin delocalisation between oxygen atoms in acetals. Here we report the results of MNDO[6,7] calculations relevant to some of these questions.

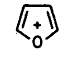
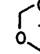
Calculations

All calculations were made using MNDO, using the published parameterization,[6,7] implemented on a VAX 11/780 computer. UHF wavefunctions were used for open shell species, and all geometries were completely optimised throughout: for a number of molecules and ions, as well as carrying out full optimisation of geometry, the effect of imposing selective symmetry constraints was also investigated.

Results and Discussion

Free optimisation of the geometry of Me_2O^+ gave a structure of C_{2v} symmetry at the energy minimum; however, the barrier to rotation of the CH_3 groups is very small, as judged by the changes in energy when fixed conformations were employed. As expected, the $\widehat{COC}$ angle was calculated to be larger than in the neutral molecule. The proton spin density (see Table 1) was calculated as 0.048, similar to that calculated for the neutral MeO· radical, 0.049; these values are reasonably consistent with the values found for the hyperfine couplings in frozen solutions, 42.3 G[1] and 52 G,[8] respectively, but quite inconsistent with the value of 23.2 G reported[9] for MeO· in the gas phase.

Table 1. Observed proton hyperfine couplings and calculated proton spin densities

Radical	$A(^1H)/G$ [a]	$\rho(^1H)$	
Me_2O^+	42.3 (6 H) [b]	0.048	
MeO·	52 (3 H) [c]	0.049	
Et_2O^+		0.073 (CH_2)	
		−0.003 (CH_3)	
		−0.029 (α)	
		−0.001 (β)	
	65 (4 H) [b,d]	0.073 (α) [e]	
		−0.001 (β)	
	153 (2 H) [f,g]	0.200 (2 H)	
	11.2 (4 H) [f,g]	0.013 (4 H)	
	140.6 (2 H) [g]	0.208 (2 H)	
	26.3 (2 H) [g]	0.023 (2 H)	
	12.4 (2 H) [g]	0.013 (2 H)	
	—	0.002 (1 H)	
	—	−0.001 (1 H)	
	160.2 (2 H) [g]	0.197 (2 H)	
		0.029 (2 H)	
		0.018 (2 H)	
	~60 (total) [f]	0.023 (ax)	chair
		0.003 (eq)	
		0.028 (ax′)	boat
		0.001 (eq′)	

[a] G = 10^{-4} T. [b] Ref. 1. [c] Ref. 8. [d] For high-temperature limit of ring puckering (ref. 1). [e] For planar ring. [f] Ref. 3. [g] Ref. 4.

For both Me_2O^+ and Et_2O^+, hydrogen-atom transfer reactions [equations (1) and (2)] are exothermic processes (see

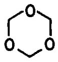
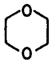
$$(RCH_2)_2O^+ \longrightarrow RCHO(H)CH_2R^+ \tag{1}$$

$$(RCH_2)_2O^+ + (RCH_2)_2O \longrightarrow R\dot{C}HOCH_2R + (RCH_2)_2OH^+ \tag{2}$$

Table 2 for calculated $\Delta H_f^\ominus$ values). The intramolecular shift [equation (1)] is more favourable for Et_2O^+ and the intermolecular shift [equation (2)] is the more favourable for Me_2O^+. For equation (1), the calculated $\Delta H^\ominus$ values are, for R = H, and CH_3, respectively, −67.2 and −84.9 kJ mol^{-1}, and for equation (2) the values are −93.7 and −11.0 kJ mol^{-1}. Both these modes of hydrogen-atom transfer have been observed experimentally,[3] and for long-chain acyclic, or medium-ring cyclic ethers have so far precluded the observation of the parent cation-radicals in frozen solutions.

For acyclic ethers, R_2O, no dimeric cation-radicals of the type $R_4O_2^+$ have yet been detected by e.s.r. spectroscopy. The present MNDO calculations indicate, however, that a weak complex of Me_2O and Me_2O^+ can exist, whose formation is exothermic by some 25 kJ mol^{-1} (*cf.* 116 kJ mol^{-1} for formation of $Me_4S_2^+$), but which is quite unlike the sulphur analogue $Me_4S_2^+$ in both geometric and electronic structure.[5,10] Whereas the dimeric species $Me_4S_2^+$ has overall C_{2h} symmetry with a calculated[10] S–S distance of 2.191 A, typical of bonding distances, the oxygen species $Me_4O_2^+$ has no symmetry and an O–O distance of 3.44 Å, while the calculated geometries of the two Me_2O fragments are scarcely perturbed from those calculated for the isolated Me_2O and Me_2O^+ species. Similarly, the electronic structure is perturbed very little by complex formation: one Me_2O fragment is essentially

Table 2. Calculated $\Delta H_f^\ominus$ values

M	$\Delta H_f^\ominus(M)$/ kJ mol^{-1}	$\Delta H_f^\ominus(M^+)$/ kJ mol^{-1}
Me_2O	−214.3	+781.1
$MeO\cdot$	−24.3	—
Et_2O	−259.3	+711.4
	−36.2	+791.4
	−248.0	+714.7
	−388.9	+613.0
	−370.4	+585.7
	−540.7	+455.7
	−356.2	+575.1 (chair) +583.9 (boat)
$(MeO)_2(CH_2)$(*c–c*)	−384.5	+626.1
(*c–t*)	−379.0	+583.1
(*t–t*)	−376.0	+607.8
(*g–g*)	−394.6[a]	*b*

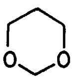
Other calculated values (kJ mol^{-1}): Me_2OH^+, +581.9; CH_3OCH_2, −108.8; $CH_3O(H)CH_2^+$, +713.2; $Me_4O_2^+$, +543.0; Et_2OH^+, +521.4; $C_2H_5OCHCH_3$, −180.3; $C_2H_5OCH_2CH_2$, −131.4; $C_2H_5O(H)CHCH_3^+$, +626.5

Experimental values[c] (kJ mol^{-1}): Me_2O, −184.0; Et_2O, −251.7; furan, −34.8; THF, −184.2; (I), −297.5; (II), −350.0; (III), −465.9; (IV), −316.0; $(MeO)_2CH_2$, −348.2; Me_2O^+, +795; Et_2O^+, +666; (furan)$^+$, +823; (THF)$^+$, +725; (I)$^+$, +669; (II)$^+$, +647; (III)$^+$, +556; (IV)$^+$, +566; $(MeO)_2CH_2^+$, +616

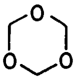
[a] Calculated dihedral angles δ(COCO) = 77.5°; experimental value, 66.3° (E. E. Astrup, *Acta Chem. Scand.*, 1973, **27**, 3271). [b] Collapses to *c–t* conformer on optimisation. [c] Experimental values from: J. B. Pedley and J. Rylance, ' Sussex-N.P.L. Computer Analysed Thermochemical Data: Organic and Organometallic Compounds,' University of Sussex (1977); H. M. Rosenstock, K. Draxl, B. W. Steiner, and J. T. Heron, ' Energetics of Gaseous Ions,' National Bureau of Standards, Washington D.C., 1977.

neutral, and its hydrogen atoms carry zero spin, but the other Me_2O fragment carries a unit positive charge with a mean spin density on the hydrogen atoms of 0.049, virtually identical with that calculated for isolated Me_2O^+ cation-radicals (see Table 1). When the O–O distance was fixed at 2.517 Å, the value found for the boat conformer of the 1,4-dioxane cation-radical (see below), the energy of $Me_4O_2^+$ was increased by only some 20 kJ mol^{-1}, *i.e.* its formation was still just exothermic; the electronic structure in this configuration is again very similar to that of the two isolated components, one having approximately zero spin on its hydrogen atoms, and the other having a mean hydrogen spin density of 0.047. Both at equilibrium and with the O–O distance fixed at 2.517 Å, the SOMO contains a significant contribution only from one oxygen atom, that in the fragment resembling Me_2O^+. Hence it is not possible to categorise this complex as a properly delocalised σ* radical analogous to $Me_4S_2^+$, nor does it seem possible that formation of such a complex could be detected by hyperfine splittings alone.

(I)



(II)



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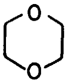

(IV)

The cation-radical derived from tetrahydrofuran [1] exhibits a temperature-dependent e.s.r. spectrum readily interpreted in terms of a puckering motion of the five-membered ring. At low temperature (77 K) the two protons in each CH_2 group adjacent to oxygen are non-equivalent, giving a triple–triplet spectrum characteristic of two different proton couplings. At higher temperature (155 K), rapid ring puckering renders these protons equivalent on the e.s.r. time scale giving a quintet spectrum characterised by a single proton coupling. Our MNDO calculations do not reproduce the non-planar ring geometry: this is not surprising in view of the small [1] (6.9 kJ mol^{-1}) barrier for the ring puckering.

However, for the planar ring, the calculations predict that the spin density is much greater at the α protons than at the β protons (see Table 1); this is consistent with the experimental e.s.r. spectrum at 155 K, where no splitting owing to the β protons was resolved (we shall return later to the relationship between calculated spin densities and observed hyperfine couplings). The SOMO in the cation-radical is a π orbital of A_2 symmetry in C_{2v}, having two nodal planes intersecting at the oxygen.

For the planar cation-radical of furan itself, which appears not to have been observed so far,* the SOMO is again of A_2 symmetry, but the four hydrogen atoms all lie in one of the nodal planes, whereas in the tetrahydrofuran cation-radical, in its planar form, the hydrogen atoms do not lie in a nodal plane of the SOMO.

The cation-radical derived from 1,3-dioxolane, (I), is calculated to be planar, with the SOMO a π orbital of B_1 symmetry in C_{2v}. (We employ the convention that in planar molecules of C_{2v} symmetry, the x axis is perpendicular to the molecular plane: consequently our B_1 orbital in this cation is equivalent to the B_2 designation used in ref. 4.) This SOMO contains large and equal contributions from both oxygen atoms, and there is a large hydrogen spin density, 0.200, calculated for the single CH_2 group between the oxygen atoms, with a much smaller value, 0.013, calculated for the other four hydrogens, which are permutationally equivalent in C_{2v} symmetry. Experimentally, a large triplet splitting is observed [3,4] having $A(^1H)$ of 153 G, with a smaller quintet splitting of 11.2 G. The ratio of the calculated hydrogen spin densities, 15.4, is tolerably close to the ratio of the experimental hyperfine couplings, 13.7.

Whereas the interpretation of the e.s.r. spectrum of the 1,3-dioxolane cation-radical is essentially straightforward, the spectrum of the cation derived from 1,3-dioxane (II) is more complex.[4] Three different hyperfine couplings occur, each involving two of the eight hydrogen atoms (see Table 1). Although geometry optimisation for the neutral molecule gives a chair conformation of overall C_s symmetry, consistent with experiment,[11] optimisation of the cation geometry leads to a structure, also of C_s symmetry, containing a planar COCOC fragment with the remaining carbon atom displaced from this plane by some 0.45 Å (for the principal geometric parameters calculated for cyclic cation-radicals, see Table 3). In the methylene group between the two oxygen atoms, the hydrogen atoms carry equal spin-densities of 0.208 (see Table 1), so that this $-O-CH_2-O-$ fragment must be associated with

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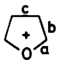
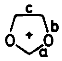
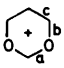
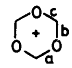
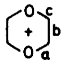
* *Note added in proof:* The cation radical of furane has recently been observed (D. N. Ramakrishna Rao and M. C. R. Symons, *J. Chem. Soc., Perkin Trans. 2*, 1983, 135): the SOMO has A_2 symmetry.

Table 3. Principal geometric parameters calculated for cyclic cation-radicals

						
					(chair)	(boat)
Distances (Å)						
a	1.408	1.367	1.355	1.361	1.382	1.381
b	1.551	1.427	1.421	1.428	1.637	1.638
c	1.547	1.566	1.543	1.397	1.382	1.381
Bond angles (°)						
aa′	114.4	108.1	117.7	115.2	121.8	121.4
ab	107.5	112.8	126.2	125.0	106.9	108.6
bc	105.3	103.1	113.2	108.1	106.9	108.6
cc′	—	—	112.8	120.9	121.8	121.4
Ring dihedral angle (°)						
	—	—	148.2 (× 1)	135.6 (× 1)	126.7 (× 2)	130.5 (× 2)

the 140.6 G coupling in the observed spectrum. The four hydrogen atoms of the other two methylene groups in the COCOC plane may be divided into an approximately axial pair having ρ(H) of 0.023 and an approximately equatorial pair having ρ(H) of 0.013: the calculated hydrogen spin densities for the out-of-plane methylene group are very small, +0.0024 for the axial hydrogen atom and −0.0011 for the equatorial. The calculated structure thus rationalises the number of distinct proton hyperfine couplings observed, and the relative magnitudes of these couplings are roughly reproduced by the calculated spin densities, allowing a definitive assignment of the e.s.r. spectrum. The observed *A* values (Table 1) are in the ratio 11.3 : 2.1 : 1.0, whereas the calculated spin densities are in the ratio 16.0 : 1.8 : 1.0. In general, for the ether and acetal cation-radicals studied in this work, there is a reasonable linear relationship between the observed $A(^1H)$ values and the calculated ρ(H) values, up to $A = 65$ G as found in the tetrahydrofuran cation, where the scale factor is in the range 850—900. For the very large couplings, the spin densities calculated by MNDO appear to be systematically overestimated.

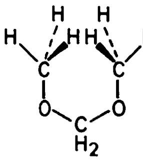
The SOMO of the 1,3-dioxane cation-radical, of *A′* symmetry, contains significant contributions from all the atoms, but the largest coefficients are associated with the oxygen orbitals normal to the COCOC plane. It is perhaps interesting that, of the non-hydrogen atoms, the smallest contributor to the SOMO is the carbon atom of the $-O-CH_2-O-$ fragment, despite the substantial contributions of the hydrogens in this fragment. Despite the non-planarity of the ring as a whole, the coefficients of the SOMO indicate that hyperconjugative delocalisation in the $-O-CH_2-O-$ fragment is not the sole mechanism available for electron delocalisation between the oxygen atoms, either in this radical, or in those derived from 1,3-dioxolane or 1,3,5-trioxane.

Closely similar to 1,3-dioxane (II) is 1,3,5-trioxane (III). The neutral molecule optimises to a chair conformation of overall C_{3v} symmetry, as found experimentally,[12] in which there are two sets, each of three hydrogen atoms, axial and equatorial. However, the e.s.r. spectrum observed[4] for the cation-radical shows strong coupling to only two protons (see Table 1). Consistent with this spectrum, and entirely analogous to the example of 1,3-dioxane, the cation-radical derived from 1,3,5-trioxane optimised to a structure of C_s symmetry in which there is again a planar COCOC fragment with the remaining oxygen atom displaced from this plane by some 0.48 Å. The methylene protons of the in-plane $-O-CH_2-O-$ fragment carry a high spin density, calculated as 0.197, and hence must be associated with the large, observed[4] hyperfine coupling; of the four remaining hydrogen atoms, those which are axial each carry a spin density of 0.029, and those which are equatorial, a spin density of 0.018. The values are all very similar to those calculated for the cation-radical of 1,3-dioxane (Table 1), and under conditions of high resolution, the e.s.r. spectra of these two cation-radicals may be expected to be very similar, both qualitatively and quantitatively. The SOMO is similar in form to that of the 1,3-dioxane cation, with all atoms again making significant contributions. The largest contributor is now the out-of-plane oxygen atom, whereas the two in-plane oxygens have much smaller coefficients; as before, the smallest contributor is the carbon atom of the in-plane $-O-CH_2-O-$ group.

The cation-radical derived from 1,4-dioxane (IV) is of especial interest as Symons and Wren[3] have suggested that, unlike the neutral parent,[13] it exists in the boat conformation, having a σ bond between the two oxygen atoms, with consequent confinement of the unpaired electron into the σ*(O−O) orbital. One of the experimental observations underlying this suggestion is the small total proton coupling: this could indicate, by comparison with the fall in $A(^1H)$ on formation of $Me_6P_2^+$ from Me_3P^+, or of $Me_4S_2^+$, the formation of an analogous σ* species.

Accordingly, we have investigated both chair and boat conformations of this radical, which in contrast to the cation-radicals derived from (II) and (III), optimise to structures of C_{2h} and C_{2v} symmetry, respectively: there are consequently no planar five-atom fragments. The chair conformer has a slightly lower $\Delta H_f^\ominus$ value (Table 2) and the geometrical parameters of the two forms are very similar with the exception of the ring conformation. More important, the calculated hydrogen spin densities are also rather similar for the two conformers. In the chair form, the axial hydrogen spin density is 0.023, and the equatorial 0.003, while in the boat form, the pseudo-axial density is 0.028 and the pseudo-equatorial density is 0.001. These values suggest, firstly, that it may be difficult to obtain definitive identification of the conformation from hyperfine couplings alone, and secondly, that the small total hydrogen spin density, manifested experimentally[3] in the small total proton coupling of 60 G, is not, in this example at least, necessarily diagnostic of formation of a σ* radical with a direct O−O interaction. Nevertheless, the O ··· O distances calculated for the two conformers do not differ greatly, being 2.517 Å in the boat form and 2.667 Å in the chair. In both conformers, the SOMO is bonding over all the non-hydrogen atoms, although in each case with a larger contribution from oxygen than from carbon; moreover, in both conformers the phase relationship between the oxygen contributions to the SOMO is calculated, in the UHF/MNDO approximation, to be σ rather than σ*.

It seemed possible from this example that electron delocalisation between oxygen atoms could in fact occur over fairly long distances. To test this point, we made calculations on the neutral and mono-positive species $CH_3O(CH_2)_nOCH_3$, for $n = 1,2,3$, in conformations that maximised the O ··· O distances. For each value of *n* studied, the top two occupied MOs of the neutral molecule are indeed found to be localised primarily on the oxygen atoms; the HOMO is an out-of-phase combination of oxygen *p* orbitals, and the next orbital an in-phase combination. Both the oxygen AO coefficients in these two MOs, and the net charges on the two oxygen atoms, are equivalent within each of the neutral molecules: the fully extended chain conformers all have a two-fold symmetry element perpendicular to the chain direction with overall C_s symmetry for $n = 1$ or 3, and C_2 when $n = 2$. On the other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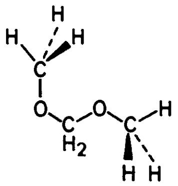
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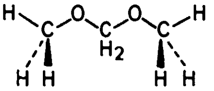
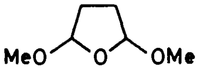

(VII)

hand, in the extended-chain conformers of the cations, the two oxygens are clearly non-equivalent, as judged both by their overall electron populations, and by their spin densities: the net charges on the oxygens range from +0.053 e and −0.325 e when $n = 1$, to +0.092 e and −0.343 e when $n = 3$. In addition, the two-fold symmetry in the molecular geometry is lost: even if this is imposed, the electronic structure still exhibits a marked asymmetry similar to that found in free optimisations. When $n = 1$, only for the all *cisoid* (V) conformer of $(MeO)_2CH_2^+$ were the two oxygens calculated to be equivalent in terms of charge, spin density, and contribution to the SOMO; this conformer, however, was *ca.* 43 kJ mol^{-1} higher in energy than the overall minimum energy conformer, the *cisoid–transoid* form of C_s symmetry (VI). In this second conformer, the calculated net charges on the oxygens are +0.010 e and −0.372 e, and the hydrogen spin densities are 0.110(×2), 0.063(×2), and 0.0009(×4); in the third, all *transoid* conformer (VII), again of only C_s symmetry and *ca.* 25 kJ mol^{-1} above the energy minimum, the calculated ρ(H) values are 0.101(×2), 0.061(×2), and 0.010(×4). The ρ(H) values in the high energy, all *cisoid*, conformer are calculated to be 0.228(×2), 0.015(×4), and 0.0002(×2). These calculated densities are to be compared with the observed[4] $A(^1H)$ values (at 133 K): 136.1 (2 H), 31.3 (2 H), and 6.0 (4 H) G. The *cisoid–transoid* conformer is the only one for which the calculated spin densities can accommodate even approximately the observed pattern of *A* values.


(VIII)

Only for the cation-radical derived from 2,5-dimethoxytetrahydrofuran (VIII) do our calculations wholly disagree with the observed spectrum.[4] The spectrum contains two different couplings from an unspecified isomeric form: 135.0 G (2 H) and 32.0 (2 H), of which the larger is most naturally assigned to the hydrogen atoms on carbons 2 and 5. The calculated structure of the *trans*-isomer has C_2 symmetry in both its geometric and electronic structure, but the hydrogen spin density is calculated to be far too low. The hydrogens on C(2) and C(5) have calculated densities of only 0.068 and the total hydrogen spin density is only 0.140. Similarly, in the *cis*-isomer, which like the $CH_3O(CH_2)_nOCH_3^+$ series is non-symmetric with net charges on the exocyclic oxygens of +0.056 e and −0.356 e (*cf.* −0.307 e in the *trans*-isomer), again it has very low hydrogen spin densities, totalling only 0.191. For any reasonable value of the MNDO scale factor between ρ(H) and $A(^1H)$, the calculated values of ρ are between ¼ and ⅓ of those required to fit the observed *A* values. At the present time, we can offer no explanation for this discrepancy.

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