

0.71)<sup>1a</sup> than that obtained in this investigation through the DSP treatment of the same system where X represents substituents capable of both polar-inductive and mesomeric effects. This inconsistency is real and cannot be ascribed to the uncertainty of the fits. If the substituent-effect analyses were correct in both cases, the  $\rho_I$  values were expected to be equal. We believe this discrepancy is inherent in the definition of  $\sigma_I$  constants, proposed as universal but having their reference in the benzene ring of the benzoic acids. We have in fact previously ascribed the enhanced  $\rho_I$  value of 3 (X represents substituents capable of polar-inductive effects only) to two factors: the greater polarizability of the aromatic ring (relative to that of toluene) and the charge transfer from nitrogen to the ring, inductively controlled by the substituent X. Because of their definition of universality, the  $\sigma_I$  constants cannot become enhanced in order to account for the above two factors, the effect of which must then show up in the enhanced  $\rho_I$  value. In the DSP treatment, instead, it is up to the mesomeric term to account for these two factors, and, consequently, the  $\rho_I$  value comes out to have a figure quite similar to that of the  $\alpha$ -substituted toluenes. Since into the mesomeric term there are poured variable (from system to system) amounts of inductively controlled terms which are not accounted for by the universal  $\sigma_I$  constants, the ratio  $\lambda = \rho_R/\rho_I$  may assign fictitious importance to polar-inductive and resonance contributions. The danger of separating polar-inductive and mesomeric contributions via statistical correlations only may be overcome by also analyzing, when possible, individual or cluster sets of raw data.

### Conclusion

Contiguous delocalization interactions between two ad-

jacent functionalities are accounted for by  $\sigma^-$  values originally devised for "direct" interactions mediated by a *p*-phenylene ring. Exceptions are noted for a few substituents having special steric constraints to full delocalization when present in a position para to the interacting group G. A set of  $\sigma_c^-$  constants is thus proposed to account for contiguous interactions between adjacent functionalities: this set overlaps with Hine's  $\sigma^-$  set for the majority of substituents but provides new values for substituents incoherent in the Hammett and iso-Hammett series. A duality of values is recognized for certain substituents depending on whether the adjacent group G is O or NH. Taking advantage of the recently proposed  $\sigma_{IB}$  set (inductive constants derived from  $\alpha$ -substituted toluenes), the scale of  $\sigma_R^-$  values based on Taft's  $\sigma_{RA}$  set is expanded and partially modified.

**Registry No.** 3 (X = H), 62-53-3; 3 (X = Ph), 122-39-4; 3 (X = CONMe<sub>2</sub>), 101-42-8; 3 (X = CO<sub>2</sub>Me), 2603-10-3; 3 (X = COMe), 103-84-4; 3 (X = COPh), 93-98-1; 3 (X = CHO), 103-70-8; 3 (X = COCF<sub>3</sub>), 404-24-0; 3 (X = NO<sub>2</sub>), 645-55-6; 3 (X = CN), 622-34-4; 3 (X = SO<sub>2</sub>Me), 1197-22-4; 3 (X = SOPh), 14933-97-2; 3 (X = SO<sub>2</sub>Ph), 1678-25-7; 3 (X = SO<sub>2</sub>NMe<sub>2</sub>), 4710-17-2; 3 (X = PO(OEt)<sub>2</sub>), 1445-38-1; 3 (X = POPh<sub>2</sub>), 6190-28-9; 3 (X = 2-py), 6631-37-4; 3 (X = 3-py), 5024-68-0; 3 (X = 4-py), 22961-45-1; 3 (X = Me), 100-61-8; 3 (X = CH<sub>2</sub>CN), 3009-97-0; 4 (X = H), 108-95-2; 4 (X = Ph), 101-84-8; 4 (X = CONMe<sub>2</sub>), 6969-90-0; 4 (X = CO<sub>2</sub>Me), 13509-27-8; 4 (X = COMe), 122-79-2; 4 (X = COPh), 93-99-2; 4 (X = COCF<sub>3</sub>), 500-73-2; 4 (X = CN), 1122-85-6; 4 (X = SO<sub>2</sub>Me), 16156-59-5; 4 (X = SO<sub>2</sub>Ph), 4358-63-8; 4 (X = PO(OEt)<sub>2</sub>), 2510-86-3; 4 (X = POPh<sub>2</sub>), 1706-96-3; 4 (X = 2-py), 4783-68-0; 4 (X = 3-py), 2176-45-6; 4 (X = 4-py), 4783-86-2; 4 (X = Me), 100-66-3; 4 (X = CH<sub>2</sub>CN), 3598-14-9; 5 (X = Ph), 92-67-1; 5 (X = CONMe<sub>2</sub>), 6331-71-1; 5 (X = CO<sub>2</sub>Me), 619-45-4; 5 (X = COMe), 99-92-3; 5 (X = COPh), 1137-41-3; 5 (X = NO<sub>2</sub>), 100-01-6; 5 (X = CN), 873-74-5; 5 (X = SO<sub>2</sub>Me), 5470-49-5; 5 (X = SO<sub>2</sub>NMe<sub>2</sub>), 1709-59-7; 6 (X = CO<sub>2</sub>Me), 99-76-3; 6 (X = COMe), 99-93-4; 6 (X = COPh), 1137-42-4; 6 (X = SO<sub>2</sub>Me), 14763-60-1.

## Stereochemistry of Tetrahydropyran-2-yl Ions, Radicals, and Related Species. Conjugative and Inductive Effects<sup>1</sup>

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The inductive effect discriminates against a planar geometry at the trivalent center in tetrahydropyran-2-yl radicals in favor of a bent geometry. Conjugation between the nonbonded carbon orbital,  $\psi$ , and the two lone-pair orbitals of the adjacent oxygen atom discriminates against both a planar geometry and a bent geometry with  $\psi$  pseudoequatorial in favor of a bent geometry with  $\psi$  pseudoaxial. The result is an asymmetrical inversion potential. Conjugation in the present model also favors a pseudoaxial  $\psi$  in the anions but favors planarity in the cations. The neglect of overlap leads to qualitatively different results for the radicals and anions. Similar results are obtained for related species.

Oxygen-substituted alkyl radicals in which the trivalent carbon atom is bonded to one or more oxygen atoms have attracted a great deal of experimental attention.<sup>2-10</sup> Both

the overall geometry of such radicals and the local geometry at the trivalent carbon are of some interest. Considerations of the inductive effect<sup>11</sup> lead to the conclusion that

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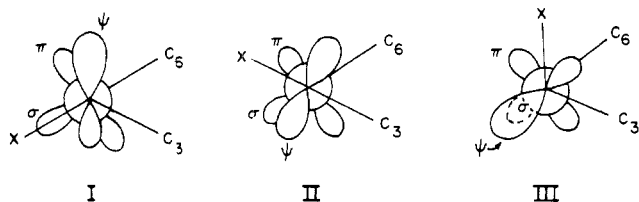
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the geometry of the planar methyl radical ( $\dot{\text{C}}\text{H}_3$ ) should become increasingly nonplanar with the successive replacement of the hydrogens with oxygens. On the other hand, conjugative delocalization of the unpaired electron onto the adjacent oxygen(s) might be expected to introduce some double-bond character into the C–O bond(s) and therefore to resist such a trend. Electron spin resonance studies<sup>4,5,9</sup> indicate that the geometry at the trivalent carbon does, however, become progressively more nonplanar as the number of nearest-neighbor oxygens increases.

In particular, measurements of  $a(\text{H}_\alpha)$  and  $a(^{13}\text{C}_\alpha)$  indicate that the 1,3-dioxan-2-yl radical is considerably more bent at the radical center than its 1,4 and 1,5 isomers and the tetrahydropyran-2-yl radical.<sup>4,5</sup> However, two bent geometries are possible and the geometrical constraints imposed on these radicals by cyclicity and the nonplanarity of the rings together ensure that they are not equivalent. More specifically, the nonbonded carbon orbital,  $\psi$ , can be either pseudoaxial or pseudoequatorial, one of these geometries must be more stable than the other, and the inversion potential at the trivalent center must be asymmetric.

The results of a recent EPR study of 2-alkoxytetrahydropyran-2-yl radicals have been interpreted to mean that the conformer with  $\psi$  pseudoaxial is in fact the more stable one.<sup>10</sup> This constitutes a reversal of the anomeric effect in the parent molecules.<sup>12</sup> At first sight, it is tempting to attribute the radical's conformational preference to repulsion between the substituents at the 2, 4, and 6 positions. This obviously favors the conformer with  $\psi$  pseudoaxial, but an estimate (0.6 kcal/mol) of the size of this effect shows that it is too small to account for the experimentally estimated enthalpy difference ( $\geq 1.5$  kcal/mol) between the two conformers.<sup>10</sup> Clearly, more subtle factors are at work. An examination of the interactions between  $\psi$  and the ring quickly leads to the conclusion that those between  $\psi$  and the lone pairs of the ring oxygen are likely to be the principal ones in which  $\psi$  is involved. The purpose of this article is to show that, if due allowance is made for the energetic and orientational nonequivalence of the two oxygen lone pairs<sup>13</sup> and for overlap, these interactions lead naturally to a preference for a pseudoaxial  $\psi$ . The interaction energies are calculated in a simple, well-known perturbation model which utilizes an effective one-electron Hamiltonian. Results obtained in the same model for the cation and anion are also reported. The model is easily extended to related species with an additional ring or exocyclic nearest-neighbor oxygen. The three possible orientations of  $\psi$  relative to the  $\pi$  and  $\sigma$  lone-pair orbitals of the oxygen atom in the tetrahydropyran-2-yl ring are shown in I ( $\psi$  pseudoaxial), II ( $\text{C}_3\text{C}_2\text{X}$  coplanar), and III ( $\psi$  pseudoequatorial). Since



both  $\sigma$  and  $\pi$  lie at lower energies than  $\psi$ , the  $\sigma \leftrightarrow \psi$  and

$\pi \leftrightarrow \psi$  interactions stabilize  $\sigma$  and  $\pi$  and destabilize  $\psi$ . To second order in perturbation theory (including overlap), the total stabilization energy for the lone-pair orbitals is

$$2 \sum_{\phi=\pi,\sigma} [H(\psi;\phi) - S(\psi;\phi)\epsilon_\phi]^2 / (\epsilon_\psi - \epsilon_\phi) \quad (1)$$

and the total destabilization energy for the nonbonded orbital is

$$n \sum_{\phi=\pi,\sigma} [H(\psi;\phi) - S(\psi;\phi)\epsilon_\phi]^2 / (\epsilon_\psi - \epsilon_\phi) \quad (2)$$

where  $H(\psi;\phi) = \langle \psi | H' | \phi \rangle$ ,  $S(\psi;\phi) = \langle \psi | \phi \rangle$ , the  $\epsilon$ 's are the energies of the unperturbed orbitals, and  $n$  ( $=0, 1, 2$ ) is the number of electrons formally associated with the trivalent carbon. Since the resonance integrals can be expressed approximately in terms of the corresponding overlap integrals and the  $\epsilon$ 's, sums 1 and 2 can be evaluated once the functional forms and the energies of the unperturbed orbitals and the geometrical parameters are specified.

Our present purpose does not require the sums to be evaluated accurately, and therefore representative, but realistic, expressions, functions, and parameters should be adequate. We chose the Wolfsberg–Helmholz formula<sup>14</sup>

$$H(\psi;\phi) = \frac{1}{2}K(\epsilon_\psi + \epsilon_\phi)S(\psi;\phi) \quad (3)$$

took the unperturbed orbitals to be Slater-type 2p orbitals with exponents given by Slater's rules, and put  $K = 1.75$ .<sup>15</sup> We took  $r_{\text{C-O}}$  to be the C–O bond length (1.434 Å) observed for methanol;<sup>16</sup> that (1.423 Å) observed for 1,4-dioxane<sup>17</sup> is negligibly different. We set dihedral angle  $\text{C}_3\text{C}_2\text{OC}_6 = 60^\circ$  and assumed tetrahedral geometries at  $\text{C}_2$  in I and III and that  $\sigma$  makes an angle of  $120^\circ$  with the  $\text{C}_2\text{O}$  bond.

Due to the lack of ionization potential (IP) data for suitable reference molecules and to the difficulty of identifying such systems, the energies of the unperturbed orbitals are more difficult to estimate.  $\epsilon_\psi$  was put equal to the negative of the IP (8.38 eV) observed for the ethyl radical.<sup>18</sup> Measured IP's for the oxygen lone pairs of the two ethers oxetane and dimethyl ether are as follows: oxetane,<sup>19</sup> 9.63 ( $\pi$ ) and 12.0 ( $\sigma$ ); dimethyl ether,<sup>20</sup> 10.04 ( $\pi$ ) and 11.93 ( $\sigma$ ). David et al.<sup>21</sup> cite a private communication from P. D. Mollere and H. Bock that photoelectron studies on tetrahydropyran show that the  $\sigma$  pair is at least 1.35 eV more stable than the  $\pi$  pair. They also report that an ab initio calculation on tetrahydropyran gave a splitting of 17 kcal/mol. On the basis of these results, we put  $\epsilon_\pi = -10.0$  and  $\epsilon_\sigma = -11.35$  eV. However, the IP of the  $\pi$  pair in tetrahydropyran has in fact been measured to be 9.50 eV.<sup>22</sup> Had we used this value, the trends already apparent in our results (Table I) would have been more pronounced.

These results, which should be given qualitative significance only, suggest that conjugative delocalization between  $\psi$  and the oxygen lone-pair orbitals favors a planar cation and a radical and anion with  $\psi$  pseudoaxial. The smaller electronegativity difference between  $\text{C}^+$  and O than between C and O will also favor a cation that is less bent

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Table I. Interaction Energies (kcal/mol) between  $\psi$  and the Oxygen Lone Pairs

	S	n = 0			n = 1			n = 2		
		$\psi \leftrightarrow \pi$	$\psi \leftrightarrow \sigma$	total	$\psi \leftrightarrow \pi$	$\psi \leftrightarrow \sigma$	total	$\psi \leftrightarrow \pi$	$\psi \leftrightarrow \sigma$	total
I	$\neq 0$	-13.4	-0.04	-13.4	-2.64	0.01	-2.63	8.07	0.05	8.08
	0	-93.5	-0.36	-93.9	-46.7	-0.18	-46.9	0	0	0
II	$\neq 0$	-5.02	-10.7	-15.7	-0.99	1.37	0.38	3.03	13.40	16.4
	0	-35.1	-90.9	-126.0	-17.5	-45.5	-63.0	0	0	0
III	$\neq 0$	0	-13.9	-13.9	0	1.79	1.79	0	17.5	17.5
	0	0	-118.8	-118.8	0	-59.4	-59.4	0	0	0

than either the radical or the anion. On the other hand, the larger electronegativity difference between C<sup>-</sup> and O than between C and O will favor an anion that is more bent than the radical. In both the cation and the radical, there is a net transfer of charge from the oxygen atom to the trivalent carbon. Like the presence of the second electron in  $\psi$  in the anion, this favors bending because nonplanarity reduces the interelectron repulsion around the trivalent carbon. As noted before, steric interactions across the ring also favor I, but their magnitude indicates that they play a secondary role.<sup>10</sup>

The  $\psi \leftrightarrow$  lone pair interactions in the radical are examples of three-electron, two-orbital bonds. The properties of such bonds have been discussed elsewhere.<sup>23-27</sup> The three-electron bond formed between  $\psi$  and  $\pi$  is stabilizing and the stabilization energy increases in magnitude with overlap in the present range. Reflecting the larger energy gap,<sup>24-26</sup> the three-electron bond formed between  $\psi$  and  $\sigma$  is destabilizing and the destabilization energy increases in magnitude with overlap. However, because the overlap integrals  $S(\psi;\pi)$  and  $S(\psi;\sigma)$  vary in opposite directions with the inversion coordinate, both bonds favor I. The present model indicates that the  $\psi^1 \leftrightarrow \sigma$  interaction energy can be as big as the  $\psi^1 \leftrightarrow \pi$  interaction energy. The  $\psi^1 \leftrightarrow \sigma$  interaction therefore cannot be neglected as previously assumed.<sup>9,10</sup> Brunton et al.<sup>9</sup> reasoned on the basis of photoelectron results for the group 6 hydrides (see ref 28 and references cited therein) that the  $\pi$  and  $\sigma$  pairs are separated by at least 10 eV and that the  $\psi^1 \leftrightarrow \sigma$  interaction can therefore be neglected. In these studies the  $\sigma$  lone pair was identified with the s-type oxygen inner-valence electron pair, which, no matter what its energy, cannot in fact influence the direction of bending because of its spherical symmetry.

As in other instances,<sup>24-26,29-33</sup> neglecting overlap gives quite different results (Table I). Initially, the most striking aspect of the zero-overlap results is that the  $S = 0$  interaction energies for  $n = 0$  and 1 are 1-2 orders of magnitude larger than their  $S \neq 0$  counterparts. Then one notices that, in the case of the radical, the  $\psi \leftrightarrow \sigma$  interaction becomes a stabilizing interaction, the planar conformer is favored over the two bent conformers, and III is stabilized more than I. Calculations on the related 1,4-dioxan-2-yl

radical in the INDO model<sup>34</sup> also suggest that the conformer with  $\psi$  pseudoequatorial is the more stable one.<sup>8b</sup> In the case of the anion, the zero-overlap approximation leads to the conclusion that in the present model conjugative delocalization does not contribute any asymmetry to the inversion potential at C<sub>2</sub>. These results reflect of course the well-known properties of  $N(= 3, 4)$ -electron bonds in the Hückel model.

The present model is relevant to the hydroxymethyl, CH<sub>2</sub>OH, and methoxymethyl, CH<sub>3</sub>OCH<sub>2</sub>, radicals. Although no direct experimental evidence is available for the geometries of these species, line width alternation in their EPR spectra suggests that rotation about the C-O bond is restricted.<sup>2,3,6</sup> This implies that the two methylene protons in each of the two rotamers are not equivalent. Our model is consistent with the usual assumption that the COH and COC planes are coincident with  $\psi$ 's nodal plane. This conclusion is supported by ab initio calculations on CH<sub>2</sub>OH which also indicate that the barriers to rotation cannot be understood in terms of the  $\psi \leftrightarrow$  lone pair interactions alone.<sup>24</sup>

There is an important qualitative difference between the hydroxy- and methoxymethyl radicals and tetrahydropyran-2-yl radicals. In the acyclic radicals, the  $\psi$  and  $\pi$  orbitals are parallel and pyramidalization decreases their overlap. However, in the cyclic radicals,  $\psi$  and  $\pi$  are not parallel when the radical center is planar (II) due to the geometrical constraints on these systems. Pyramidalization in the axial direction (I) decreases the dihedral angle between  $\psi$  and  $\pi$  and increases their overlap. At the same time, the dihedral angle between  $\psi$  and  $\sigma$  increases and their overlap decreases. The reverse holds for pyramidalization in the equatorial direction (III). In the present model, the three-electron  $\psi \leftrightarrow \pi$  and  $\psi \leftrightarrow \sigma$  bonds are stabilizing and destabilizing, respectively. Conjugation thus joins with the inductive effect in promoting pyramidalization in the axial direction but opposes pyramidalization in the equatorial direction.

The introduction of a second nearest-neighbor oxygen at the trivalent carbon center in tetrahydropyran-2-yl radicals is expected to result via the inductive effect in an increase in nonplanarity at this center.<sup>11</sup> The effect of conjugation between  $\psi$  and the lone-pair orbitals of the second oxygen will depend on whether it is inside or outside the ring. Thus, in 1,3-dioxan-2-yl ions and radicals,  $\psi$  interacts with the symmetric combination of the two lone-pair orbitals. In the present model, this simply leads to a doubling of the interaction energies shown in Table I so that the trends already discerned for the tetrahydropyran-2-yl species become more pronounced. Surprisingly, INDO calculations on the 1,3-dioxan-2-yl and the 1,3,5-trioxan-2-yl radicals also predict that the bent conformer with  $\psi$  pseudoaxial is the more stable one.<sup>8b</sup> Conjugation between  $\psi$  and the lone pairs of a 2-alkoxy substituent will lead to larger or smaller inversion barriers than expected

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on the basis of the inductive effect alone but cannot influence the asymmetry of the inversion potential because rotation about the exocyclic C–O bond is relatively free.

Ab initio calculations have been reported for model  $\alpha$ -oxa and  $\alpha$ -thia carbanions.<sup>35</sup> These calculations, unlike the present ones, suggest that equatorial-type carbanions are more stable than axial-type carbanions. This stereoelectronic effect was attributed to the stabilizing interaction between the carbanion lone pair and the antibonding  $\sigma^*$  orbital of the antiperiplanar X–C bond in the equatorial form and to the destabilizing interaction between the carbanion lone pair and the antiperiplanar lone pair of the  $\alpha$ -heteroatom in the axial form. The former interaction is much less important in the oxygen compounds because the  $\sigma^*_{\text{CO}}$  orbital lies too high in energy to stabilize the resultant carbanion significantly.<sup>36</sup> Thus 1,3-dithiane reacts with strong base to form a carbanion, but its oxygen counterpart does not.<sup>37</sup> Since the ab initio calculations overestimate the energy of the carbanion lone pair, it follows that they underestimate the C<sup>-</sup>– $\sigma^*_{\text{CX}}$  energy gap and hence overestimate the stabilization resulting from the interaction between these orbitals. It also appears that the results of the ab initio calculations have been interpreted in terms of two energetically and orientationally equivalent  $\text{sp}^3$  lone pairs. Our work is therefore not directly comparable with the earlier ab initio work.<sup>35</sup>

The present model neglects the  $\psi$  and  $\text{C}_2\text{X}$  bond orbital  $\leftrightarrow \text{OC}_6$  bond orbital interactions and the  $\text{C}_2\text{X}$  bond orbital  $\leftrightarrow$  lone pair interactions. These interactions are the only other ones which influence the inversion potential at  $\text{C}_2$ . The one- and two-electron interactions among them are expected to play a minor role because the interaction energy is inversely proportional to the energy difference between the unperturbed orbitals and these energy differences are significantly larger than  $\epsilon_\psi - \epsilon_\phi$ ,  $\phi = \sigma, \pi$ . Only one of the remaining interactions,  $\psi^1 \leftrightarrow \sigma_{\text{OC}_6}$ , is a three-electron interaction and it occurs of course only in the radical. Due to the large energy gap between  $\psi$  and  $\sigma_{\text{OC}_6}$ , it is expected to have a destabilizing influence, and since  $S(\psi, \sigma_{\text{OC}_6})$  is probably larger in conformer III than in conformer I, it is likely that it acts in the same direction as the  $\psi \leftrightarrow$  lone pair interactions. The rest of the interactions are four-electron interactions and net destabilizing.<sup>21,38</sup> In the present perturbation model, the total four-electron interaction energy,  $\text{IE}_4$ , between two orbitals  $\mu$  and  $\nu$  is<sup>21</sup>

$$\text{IE}_4 = 4S(-H + \epsilon_0 S) \quad (4)$$

where  $H = \langle \mu | H' | \nu \rangle$ ,  $S = \langle \mu | \nu \rangle$ ,  $\epsilon_0 = 1/2(\epsilon_\mu + \epsilon_\nu)$ . Substituting (3) into (4), we find that (4) reduces to

$$\text{IE}_4 = 4(1 - K)S^2\epsilon_0 \quad (5)$$

Thus, in the present model,  $\text{IE}_4$  is directly proportional

to the square of the overlap and to the mean of the unperturbed energies.<sup>26,36,39–41</sup> Since  $\epsilon_0$  is fixed for each interaction, its contribution depends only on  $S$ . For  $K = 1.75$  and for a pair of realistic values of  $S$  and  $\epsilon_0$ , say 0.1 and  $-10$  eV, respectively,  $\text{IE}_4 \approx 7$  kcal/mol and is chemically significant. It follows from (5) that  $\sigma_{\text{C}_2\text{X}^2} \leftrightarrow \sigma_{\text{OC}_6}^2$  and  $\sigma_{\text{C}_2\text{X}^2} \leftrightarrow \sigma$  probably favor III over I and that  $\sigma_{\text{C}_2\text{X}^2} \leftrightarrow \pi$  acts in the opposite direction. The one remaining four-electron interaction,  $\psi^2 \leftrightarrow \sigma_{\text{OC}_6}^2$ , occurs  $\sigma_{\text{C}_2\text{X}^2}$  in the anion and it probably favors I over III.

Although we cannot rule out the possibility, it does not seem likely that the inclusion of these interactions in the model would overturn our conclusions based on the  $\psi \leftrightarrow$  lone pair interactions alone. Nevertheless, their neglect does constitute a deficiency of the present model. The model is also deficient in other respects. First, it has been assumed, as in other one-electron discussions<sup>21,42</sup> of conjugative delocalization and hyperconjugation, that  $\psi$  and  $\epsilon_\psi$  are independent of  $n$ . Since we put  $-\epsilon_\psi$  equal to the IP of a radical, the present calculations should be more reliable for the radicals than for the ions. Second, the admixture of the  $\text{C}_{2s}$  orbital into  $\psi$  in the nonplanar geometries has also been neglected. This stabilizes  $\psi$  and hence reduces the energy separation between  $\psi$  and the oxygen lone pairs. However, since  $\epsilon_\psi - \epsilon_\pi < \epsilon_\psi - \epsilon_\sigma$ , this effect is likely to stabilize I more than III. It might also happen that the two bent conformers are more stabilized or less destabilized by the  $\psi \leftrightarrow$  lone pair interactions than the planar conformer. Third, we have neglected the inductive effect of the adjacent heteroatoms on  $\epsilon_\psi$ . This will lower  $\epsilon_\psi$  and diminish the  $\psi \leftrightarrow$  lone pair energy gaps, but is unlikely to lead to any qualitative changes in the results. Fourth, the  $\sigma$  orbital contains some s character and is therefore not a pure 2p orbital. Finally,  $\psi$ ,  $\pi$ , and  $\sigma$  are not localized atomic orbitals but are delocalized over the ring.

In the case of the radicals, highly polar solvents will stabilize both  $\pi$  and  $\sigma$  more than  $\psi$ ,  $\epsilon_\psi - \epsilon_\pi$  and  $\epsilon_\psi - \epsilon_\sigma$  will therefore increase, and, as in the parent molecules with electronegative substituents at the 2 position,<sup>43</sup> a decrease in conformational preference should be observed.

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