

kcal/mol. The lower value for $1(C_s)$ can be attributed to significant hyperconjugation with the C1C6, C6C7, and C7C8 bonds in the isolated ion. This is revealed in the relatively high ϵ_L for $1(C_s)$ as compared to isopropyl (-7.15 eV) and cyclopentyl (-6.88 eV) and by the lengthening of the hyperconjugating bonds in $1(C_s)$ as compared to $1(C_{2v})$, viz., Figures 1 and 2. The hyperconjugation may be responsible for the moderate rate enhancement observed during acetolysis of 9-homocubyl tosylate.³ The interactions should be stronger than in 7-norbornyl cation, for example, since the hyperconjugating bonds in **1** are more strained and are in cyclobutyl rings.

The low $Q_L(C^+)$'s and high ϵ_L 's for **2**, **4**, and **5** attest to the extreme delocalization in these species. The result is ΔE_s^{est} values that fall below the hydrogen bond energies (~ 7 kcal/mol), so these ions prefer coordination of HCl with hydrogen rather than carbon. Thus, this analysis also finds that the delocalized ions are not expected to bond as strongly to a counterion or molecule in an ion pair as the more localized species, **1**. In addition, the same factors, delocalization and high LUMO energy, should lead to small substituent effects for solvolyses that generate the delocalized ions. This prediction has been verified for **5**.⁷

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Supplementary Material Available: Listing of the calculated coordinates of all atoms for **1**, **2**, **4**, and **1-CIH** (2 pages). Ordering information is given on any current masthead page.

References and Notes

- (1) Chemical Consequences of Orbital Interactions. 8. Part 7: ref 2b.
- (2) (a) W. L. Jorgensen, *J. Am. Chem. Soc.*, **99**, 280 (1977); (b) W. L. Jorgensen and J. E. Munroe, *Tetrahedron Lett.*, 581 (1977).
- (3) (a) P. v. R. Schleyer, J. J. Harper, G. L. Dunn, V. J. DiPasquo, and J. R. E. Hoover, *J. Am. Chem. Soc.*, **89**, 698 (1967); (b) R. E. Leone and P. v. R. Schleyer, *Angew. Chem., Int. Ed. Engl.*, **9**, 860 (1970).
- (4) J. C. Barborak and R. Pettit, *J. Am. Chem. Soc.*, **89**, 3080 (1967).
- (5) Reference 3b, footnote 39.
- (6) For a recent review, see: D. J. Raber, J. M. Harris, and P. v. R. Schleyer, "Ions and Ion Pairs in Organic Reactions", Vol. II, M. Szwarc, Ed., Wiley-Interscience, New York, N.Y., 1974.
- (7) R. M. Coates and E. R. Fretz, *J. Am. Chem. Soc.*, **97**, 2538 (1975); (b) W. L. Jorgensen, *Tetrahedron Lett.*, 3033 (1976); (c) H. C. Brown and M. Ravindranathan, *J. Am. Chem. Soc.*, **99**, 299 (1977); (d) R. M. Coates and E. R. Fretz, *ibid.*, **99**, 297 (1977).
- (8) (a) W. L. Dilling, C. E. Reinke, and R. A. Plepys, *J. Org. Chem.*, **34**, 2605 (1969); **37**, 3753 (1972); W. L. Dilling, R. A. Plepys, and R. D. Kroening, *J. Am. Chem. Soc.*, **91**, 3404 (1969); **92**, 3522 (1970); **94**, 8133 (1972).
- (9) W. G. Dauben and D. L. Whalen, *J. Am. Chem. Soc.*, **88**, 4739 (1966); **93**, 7244 (1971).
- (10) G. A. Olah, G. K. S. Prakash, and G. Liang, *J. Org. Chem.*, **41**, 2820 (1976).
- (11) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, **97**, 1285 (1975), and accompanying papers.
- (12) W. L. Jorgensen, *Tetrahedron Lett.*, 3029 (1976).
- (13) W. G. Dauben, C. H. Schallhorn, and D. L. Whalen, *J. Am. Chem. Soc.*, **93**, 1446 (1971); L. A. Paquette and R. S. Beckley, *ibid.*, **97**, 1084 (1975); L. A. Paquette, J. S. Ward, R. A. Boggs, and W. B. Farnham, *ibid.*, **97**, 1101 (1975), and accompanying papers.
- (14) M. Brookhart, R. K. Lustgarten, and S. Winstein, *J. Am. Chem. Soc.*, **89**, 6352 (1967).
- (15) W. L. Jorgensen, *J. Am. Chem. Soc.*, **97**, 3082 (1975).
- (16) For a review see: H. Hogeveen and P. W. Kwant, *Acc. Chem. Res.*, **8**, 413 (1975).
- (17) In this context, we would like to recommend a naming convention for the pyramidal carbocations. The system proposed by Cotton¹⁸ for organometallic complexes may be used. Thus, positions of attachment of the bridging group to the diene are given, followed by the term tetrahapto, the name of the diene, and the name of the bridging group. Then, **4** is 3,4,7,8-tetrahapto-tricyclo[4.2.0.0^{2,6}]octadienemethyl cation and pyramidal $(CH)_6^+$ is tetrahapto-cyclobutadienemethyl cation. The nomenclature may also be extended to pyramidal cations, in which π systems other than dienes are bridged. For example, Hogeveen's dictation¹⁶ is pentahapto-cyclopentadienylmethyl dication.
- (18) F. A. Cotton, *J. Am. Chem. Soc.*, **90**, 6230 (1968).
- (19) (a) R. A. Sneen, G. R. Felt, and W. C. Dickason, *J. Am. Chem. Soc.*, **95**, 638 (1973); (b) D. Darwish, S. H. Hul, and R. Tomlinson, *ibid.*, **90**, 5631 (1968).
- (20) The stabilization energies of methyl cation by HCl and HCOOH are 53^{2a} and 87 kcal/mol, respectively, according to MINDO/3. The experimental value for the former quantity is 51 kcal/mol.²¹
- (21) D. Holtz, J. L. Beauchamp, and S. D. Woodgate, *J. Am. Chem. Soc.*, **92**, 7484 (1970).
- (22) T. B. McMahon and P. Kebarle, *J. Am. Chem. Soc.*, **98**, 3399 (1976).
- (23) The LUMO of **4** resembles the π_4^* orbital of the diene.
- (24) As noted in ref 2a, the calculated hydrogen bond energies with HCl are expected to be uniformly too large by ca. 4–5 kcal/mol.
- (25) The $i\text{-Pr}(\text{HCl})_2^+$ complex is found to be unsymmetrical, though each HCl is coordinated with both the carbonium carbon and its hydrogen.
- (26) The recent results of Davidson and Kebarle²⁷ are notable in this regard, although they apply to substantially different ions. In an elegant ICR experiment they found the solvation energy difference for isoelectronic alkali cations and halide anions in acetonitrile is largely established after the addition of only four or five solvent molecules to the free ions. Contributions from outer solvent spheres, a topic along with entropy that we have not discussed here, are apparently similar.
- (27) W. R. Davidson and P. Kebarle, *J. Am. Chem. Soc.*, **98**, 6125 (1976).
- (28) Using a simple electrostatic model, similar qualitative conclusions have been reached concerning the solvation of ethyl cations: D. T. Clark, *23rd IUPAC Proc.*, **1**, 31 (1971); D. T. Clark and D. M. J. Lilley, *Tetrahedron*, **29**, 845 (1953).

A New, Simple ab Initio Pseudopotential for Use in Floating Spherical Gaussian Orbital Calculations. 2. Some Results for Hydrocarbons

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Abstract: A recently proposed model potential scheme is used to replace the 1s core orbitals for carbon in FSGO calculations. Comparisons with all-electron FSGO results indicate good agreement for C_2H_6 , C_2H_4 , C_2H_2 , C_3H_6 (cyclopropane), and $LiCH_3$.

The floating spherical Gaussian orbital (FSGO) model^{2b} allows one to perform simple ab initio electronic structure calculations without great expenditure of computational effort. At the same time it allows for easy visualization of the sepa-

ration between the behavior of the core and the valence orbitals. The pseudopotential approach to electronic structure calculations is based on just such a separation between the core and valence regions. This leads one to question whether the two

Table I. Model Potential Parameters (au) (cf. eq 1, 2b)

	α	β	$\epsilon_{2s}-\epsilon_{1s}$	n
C	12.0	2.75	10.624	0
Li ^a	3.13	1.70	2.2653	2

^a Reference 2a.**Table II.** Optimized Geometries for Hydrocarbons (Distances in au)

Molecule property	Model potential	FSGO ^a	Obsd ^b
Methane			
R_{C-H}	2.113	2.107	2.065
Ethane(staggered)			
R_{C-C}	2.843	2.836	2.899
R_{C-H}	2.119	2.117	2.065
$\angle H-C-H$, deg	107.97	108.2	109.1
Ethane(eclipsed)			
R_{C-C}	2.864	2.859	
R_{C-H}	2.109	2.114	
$\angle H-C-H$, deg	107.96	107.7	
Ethylene			
R_{C-C}	2.556	2.554	2.527
R_{C-H}	2.075	2.081	2.052
$\angle H-C-H$, deg	118.82	118.7	117.3
Acetylene			
R_{C-C}	2.289	2.296	2.277
R_{C-H}	2.032	2.039	2.001
Cyclopropane			
R_{C-C}	2.888	2.897	2.854 ^c
R_{C-H}	2.114	2.108	
$\angle H-C-H$, deg	113.84	114.4	

^a A. A. Frost and R. A. Rouse, *J. Am. Chem. Soc.*, **90**, 1965 (1968).^b L. E. Sutton, Ed., *Chem. Soc., Spec. Publ.*, No. 18 (1965). ^c J. Bastiansen, F. N. Fritsch, and K. Hedberg, *Acta Crystallogr.*, **17**, 538 (1964).

schemes (FSGO and pseudopotential) may be used together. Some calculations of FSGO-pseudopotential type have already been reported by a number of workers,³⁻⁶ and the results have, in general, been rather unsatisfactory, yielding substantial errors when compared either to all-electron FSGO calculations or to experiment. The most satisfactory FSGO pseudopotential has been that developed by Barthelat and Durand³ using the Simons' pseudopotential, but even this has two serious drawbacks: First, it is semiempirical (based on experimental ionization potentials) whereas the FSGO procedure is entirely ab initio. Second, it gives poor predictions for the geometries of molecules containing atoms at either end of the first row. We have suggested^{2a,6} that the advantages of the Simons potential compared to more elaborate Hartree-Fock-type pseudopotentials may arise from its very simple form, which does not have the elaborate functional dependence on the radial distance which is characteristic of the Hartree-Fock-type potentials; the less structured potential should be more in balance with the rather crude description of the valence electronic structure provided by FSGO.

Based on the supposition that a model potential without detailed structure would work best within the FSGO framework, we recently proposed a method^{2a} for determining an ab initio model potential for use in conjunction with FSGO calculations. In the present article we develop such a potential for the carbon atom and perform some test calculations in an FSGO framework. The form of the model potential used is

$$V^{\text{model}} = V_p(r) + V_{s-p}(r)P_{l=0} \quad (1)$$

Table III. Orbital Energies for Ethane in the Staggered Configuration (au)

Orbital	Model potential	FSGO	Ab initio SCF ^a
$1e_g$	-0.352	-0.357	-0.485
$3a_{1g}$	-0.363	-0.367	-0.493
$1e_u$	-0.459	-0.464	-0.601
$2a_{2u}$	-0.815	-0.733	-0.836
$2a_{1g}$	-1.023	-0.947	-1.021

^a S. Topiol, M. A. Ratner, and J. W. Moskowitz, unpublished results, using double- ζ quality basis set, performed at the experimental geometry.where P_l is the angular momentum projection operator and

$$V_p = \frac{-n_c}{r} e^{-ar^2} \quad (2a)$$

$$V_{s-p} = \frac{(\epsilon_{2s} - \epsilon_{1s})}{r^n} e^{-\beta r^2} \quad (2b)$$

where n_c is the number of core electrons, ϵ_{1s} and ϵ_{2s} are the 1s and 2s orbital energies,⁸ and α , β , and n are parameters.The parameters α and β are optimized sequentially. One first replaces V_{s-p} in eq 2b with a Phillips-Kleinman¹¹ type core projection operator:

$$(\epsilon_{2s} - \epsilon_{1s})|\varphi_{1s}\rangle\langle\varphi_{1s}| \quad (3)$$

where for φ_{1s} one uses a STO-3G expansion. Then α is varied so as to give the best agreement with the all-electron FSGO results for the C-H bond distance in CH₄. Having determined α , eq 3 is now changed back to eq 2 and β is optimized in the same way. This solution is obviously not unique, since two parameters, α and β , are used to match one datum, the C-H distance. The sequential method employed does, however, yield unique values; this crude procedure is found to be sufficient for the FSGO potentials.

Results and Discussion

The parameters for the model potential are given in Table I. These have been adjusted to give good agreement with the all-electron FSGO calculations for methane. In Table II we present the optimized geometries obtained using this model potential for various hydrocarbons. The agreement with all-electron FSGO results is quite good. For CH₄ this is not surprising since CH₄ was used to optimize the potential. In ethane the carbon atom is still in an almost tetrahedral environment, and one can see how well the model describes the C-C bond (i.e., the interaction of two carbon potentials). Ethylene and acetylene serve as a test of the potential in an unsaturated environment. In these cases the C-C bonding orbitals were handled exactly as in the all-electron FSGO calculations⁹ (placing them 0.1 and 0.2 units off the C-C axis for ethylene and acetylene, respectively). The cyclopropane calculations test the potential in a strained environment.

Table III contains the orbital energies for ethane in the staggered configuration. The upper three orbital energies ($1e_g$, $3a_{1g}$, $1e_u$) are in good agreement with FSGO energies. The other two orbital energies (the $2a_{1g}$ and $2a_{2u}$ orbitals, which are primarily the (carbon 2s)-(carbon 2s) bonding and antibonding pair) are seen to be much closer to the ab initio results than to the full FSGO (no model potential) results. This has been found to be a general trend.¹⁰ To understand this, we recall that in the construction of the potential, the V_{s-p} part of the potential was modeled after the Phillips-Kleinman¹¹ core projection term:

$$(\epsilon_{2s} - \epsilon_{1s})|\varphi_{1s}\rangle\langle\varphi_{1s}| \quad (3)$$

Table IV. Optimized Geometry for LiCH₃ (Distances in au)

	Model potential	FSGO (frozen 1s core)	Ab initio ^a
<i>R</i> _{C-Li}	3.482	3.613	3.819
<i>R</i> _{C-H}	2.195	2.188	2.058
∠H-C-H, deg	96.66	96.34	105.8

which tends to preserve the proper valence energy. Thus the 2a_{1g} and 2a_{2u} orbitals, which sample this part of the potential most heavily, give improved orbital energies.

Finally, in Table IV we present the results of calculations on LiCH₃ where for Li we have used the model potential developed earlier (ref 2a). This tests the model when two different (C, Li) potentials interact. It is seen that the agreement of C-Li bond distance is not as good as some of the previous results but is still acceptable.

Conclusion

The model potential developed in ref 2a has been shown to work quite well when used in an FSGO scheme for some organic compounds. The improvement over attempted calculations, employing more structured and more sophisticated potentials, is particularly noteworthy and seems to justify previous conclusions about the need to balance the extent of detailed structure in the description of core and valence regions. As a next step the present method may be extended to larger

atoms where greater savings over the all-electron FSGO calculations would be realized. In addition, it seems one might consider optimizing a similar model to give closer agreement with experimental rather than FSGO results. Both of these possibilities are being investigated.

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References and Notes

- (1) (a) Department of Chemistry, Northwestern University; (b) New York University; (c) Department of Chemistry and Materials Research Center, Northwestern University.
- (2) (a) S. Topiol, A. A. Frost, J. W. Moskowitz, and M. A. Ratner, *J. Chem. Phys.*, in press; (b) A. A. Frost, *J. Chem. Phys.*, **47**, 3707 (1967); H. F. Schaefer, III "Modern Theoretical Chemistry" Vol. 1, Plenum Press, New York, N.Y., 1976.
- (3) J. C. Barthelat and Ph. Durand, *Chem. Phys. Lett.*, **16**, 63 (1972); *J. Chim. Phys. Phys.-Chim. Biol.*, **71**, 505 (1974); *Chem. Phys. Lett.*, **40**, 407 (1976).
- (4) N. K. Ray and J. O. Switalski, *J. Chem. Phys.*, **63**, 5053 (1975); *Theor. Chim. Acta*, **41**, 329 (1976).
- (5) A. M. Semkow, R. A. Suthers, and J. W. Linnett, *Chem. Phys. Lett.*, **32**, 116 (1975).
- (6) S. Topiol, A. A. Frost, M. A. Ratner, and J. W. Moskowitz, *J. Chem. Phys.*, **65**, 4467 (1976); S. Topiol, A. A. Frost, M. A. Ratner, J. W. Moskowitz, and C. F. Mellus, *Theor. Chim. Acta*, in press.
- (7) G. Simons, *J. Chem. Phys.*, **55**, 756 (1972).
- (8) E. Clementi and C. Roetti, "Atomic Data and Nuclear Data Tables", Vol. 14, Academic Press, New York, N.Y., 1974.
- (9) A. A. Frost and R. A. Rouse, *J. Am. Chem. Soc.*, **90**, 1965 (1968).
- (10) S. Topiol, M. Ratner, A. A. Frost, and J. W. Moskowitz, unpublished results.
- (11) J. C. Phillips and L. Kleinman, *Phys. Rev.*, **116**, 287 (1959).

ESR, NMR, and ENDOR Studies of Partially Deuterated Phenyl Substituted Anthracenes. π - σ Delocalization

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Abstract: From the negative and positive radical ions of partially deuterated phenyl substituted anthracenes ESR and ENDOR-in-solution spectra have been recorded, which suggest that pure π -MO theories fail to describe the spin distribution in highly twisted aromatic radical ions. The observed sequence of the phenyl proton coupling constants $|a_{\text{H}}^{\text{meta}}| = |a_{\text{H}}^{\text{para}}| < |a_{\text{H}}^{\text{ortho}}|$ points to the necessity of π - σ mixing to interpret the observed data. Deuterium ENDOR resonances in solution have been detected for the first time. Sign determinations of the hfs couplings were performed using the new electron-nuclear-nuclear TRIPLE resonance technique. The synthesis of the various deuterated phenyl substituted anthracenes is described. Unambiguous assignments of the deuterated positions were performed using mass spectroscopy, ¹H and ¹³C NMR including noise- and off-resonance-decoupling techniques, respectively.

Simple π -MO calculations have proved to be successful in describing the π -electronic structure of planar aromatic hydrocarbons. For the description of hyperfine splittings (hfs) and electronic *g* factors excited molecular states with σ symmetry have to be taken into account, but in most cases only gross assumptions about the distribution and energies of the σ electrons seem to be required. Previously, Stone had shown that a linear correlation between experimentally determined *g* factors and the energy of the half-filled MO of planar aromatic radicals is expected, assuming a large energy gap between the π and σ electrons.¹ Results from photoelectron spectroscopy for a variety of aromatic molecules contradict this assumption, indicating the absence of such a large energy gap.² In molecules with lowered symmetry such as sterically over-

crowded phenyl substituted aromatic compounds, separation of π and σ electrons for symmetry reasons is no longer valid. Indeed, experimental *g* factors of nonplanar phenyl substituted aromatic radical ions, e.g., the ions of rubrene, 9,10-diphenylanthracene (1), and 9-phenylanthracene (5), do not fit Stone's correlation. Labeling of the compounds refers to Figure 1.

Recently an attempt was made to account for this by mixing the π -type MO's of the unpaired electron with σ MO's of the phenyl substituent.³ This *phenyl hyperconjugation model* is similar to the description of the conventional methyl hyperconjugation.⁴ The *g*-factor anomalies cannot be rationalized by this model owing to the neglect of large spin-orbit matrix elements resulting from π - σ mixing.^{3b} The unpaired electron