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Unrestricted Open-Shell Calculations by MINDO/3. Geometries and Electronic Structure of Radicals

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Abstract: The MINDO/3 semiempirical SCF-MO method has been expanded to an unrestricted open-shell treatment. The calculated heats of formation of radicals as well as their geometries compare reasonably well with experiment. Calculated spin densities predict the correct proton hyperfine splitting ordering for most EPR spectra.

The geometry and the electronic structure of radicals determining their chemical reactivity and spectroscopic properties is of great importance in many fields of organic chemistry.[1] Unlike in reactions where only closed-shell reactants are involved, the application of the Woodward–Hoffmann rules[2] is not clear cut[3] and calls for more detailed theoretical investigations.

Since at present reliable ab initio calculations cannot yet be carried out on larger systems of chemical interest, the chemist is forced to choose some semiempirical method for his purposes.

MINDO/3[4] has proven[5] to be the most reliable method of this type, although some shortcomings are well known and have been criticized.[5,6]

Calculated properties like energy, spin distribution, and dipole moment depend strongly upon the geometry of the species in question. This demands total geometry optimization in order to make the results independent of any arbitrary choice of geometrical variables.

To our experience, the original closed-shell program[7] fails to converge in some cases, probably since the bond order matrix in using the restricted half-electron method[8] is not invariant to small changes in geometry. Calculations failed to converge mainly for complex systems, where the number of geometrical variables was large.

Following Dewar's suggestion,[4] the MINDO/3 method has been expanded to a nonrestricted open-shell treatment, in which this difficulty has been avoided. Although this purpose was the main "driving force", nonrestricted calculations in addition feature the well-known advantages common to this approach: (a) negative spin densities (which are known to occur[9]) can be computed; (b) Koopmans' theorem[10] can be used to estimate ionization potentials; and (c) adiabatic ionization potentials of closed-shell systems can be calculated by comparing their energies with the energies of the optimized open-shell cations. Furthermore, calculations of this type might be regarded as an independent test upon the parameters used in MINDO/3.

Although the power of any semiempirical treatment lies in the computation of large systems, we shall focus mainly on small species in this communication in order to compare with experimental facts that are available.

Procedure

The derivation of the Roothaan equations for open-shell systems[11] is straightforward and can be found in any textbook.[12] Within the MINDO/3 framework, the elements of the F matrices take the following form:

$$F_{ii}{}^{\alpha} = H_{ii} + p_{ii}{}^{\beta}g_{ii} + \sum_{k \neq i}^{(m)} (p_{kk}g_{ik} - p_{kk}{}^{\alpha}h_{ik}) + \sum_{n \neq m} \gamma_{mn} \sum_{k}^{(n)} p_{kk} \qquad (1)$$

$$F_{ij}{}^{\alpha}(m,m) = (2p_{ij} - p_{ij}{}^{\alpha})h_{ij} - p_{ij}{}^{\alpha}g_{ij} \qquad (2)$$

$$F_{ij}{}^{\alpha}(m,n) = H_{ij} - p_{ij}{}^{\alpha}\gamma_{mn} \qquad (3)$$

where

$$p_{ij} = p_{ij}{}^{\alpha} + p_{ij}{}^{\beta} \qquad (4)$$

$$g_{ij} = (ii|jj) \qquad (5)$$

$$h_{ij} = (ij|ij) \qquad (6)$$

$$H_{ii} = U_{ii} - \sum_{n \neq m} C_n\gamma_{mn} \qquad (7)$$

and

$$H_{ij} = \beta_{ij}{}^{c} = S_{ij}(I_i + I_j)B_{mn} \qquad (8)$$

The symbols have their conventional meanings.[12] Analogous expressions hold for $F_{ij}{}^{\beta}$ of course. Using this notation, the total energy of a molecule is given by

Table I

	ΔH_f			ΔH_H			I_V		
Radical	Calcd	Obsd[a]	Error	Calcd[b]	Obsd[b]	Error	Calcd	Obsd[a]	Error
CH	137.9	142.4	−4.5	98.5	100.8	−2.3	9.31	11.13	−1.82
CH_2^+	314.0	333	−19	105.8	125.1	−19.3	19.77		
CH_3	40.9	33.2	7.7	99.3	103.2	−3.9	10.0	9.84	−0.16
CH_4^+	263.0	274	−11	98.8	104	−5.2	19.33		
C_2H	122.8	112	10.8	117.1	111.8	5.3	10.67	11.3[e]	−0.63
$C_2H_2^+$	297.2	317	−19.8	95.7	100.1	−4.4	18.51		
C_2H_3	62.5	65	−2.5	95.4	104.7	−8.6	9.24	9.45	−0.21
C_2H_5	18.4	25	−6.6	90.3	97.3	−7.7	9.07	8.40	0.67
$HC{\equiv}CCH_2$	70.2	75	−4.8	87.3	82.8	4.5	8.57	8.34	0.23
(CH_2CHCH_2)	36.1	30	6.1	81.7	85	−3.3	8.61	8.15	0.46
$c\text{-}C_3H_5$	49.3	68	−18.7	92.7	107.4	−14.7	9.03	8.05	0.98
$CH_3C{=}CH_2$	38.3	58	−19.7	83.9	105.2	−21.3	8.36		
$n\text{-}C_3H_7$	11.4	22.1	−10.7	90.0	98	−8.0	9.05	8.10	0.95
$i\text{-}C_3H_7$	1.9	16.8	−14.9	80.5	94.5	−14.0	8.66	7.50	1.16
$(CH_2)_2CCH_3$	32.4	21	11.4	82	77.4	4.6	8.65	8.03	0.63
$c\text{-}C_4H_7$	26.7	51.1[c]	−24.4	83.9	96.8	−12.9	8.78	7.93	0.85
$n\text{-}C_4H_9$	5.1	18.5	−13.4	87.6	98	−10.4	9.05	8.64	0.41
$s\text{-}C_4H_9$	−4.6	8.83	−13.43	72.4	94.5	−22.1	8.68	7.93	0.65
$i\text{-}C_4H_9$	12.8	12.67	0.13	89.8	98	−8.2	9.0	8.35	0.65
$t\text{-}C_4H_9$	−5.4	4.5	−9.9	71.6	91	−19.4	8.49	7.41	1.07
$c\text{-}C_5H_9$	2.8	22[d]	−19.2	82.8	92.5	−9.7	8.77	7.79	0.98
$c\text{-}C_6H_{11}$	−8.9	12[d]	−20.9	79.8	93.6	−13.8	8.71	7.66	1.05
Phenyl	69.6	72	−2.4	92.9	104	−11.1	8.81	9.20	−0.39
Benzyl	51.6	37.5	14.1	80.2	85	−4.8	8.09	7.76	0.33
Phenoxy	2.2	9	−6.8	82.8	84.1	−1.3	9.08	8.84	0.24
1-Norbornyl	43.3			87.0			8.73		
7-Norbornyl	40.8			84.5			8.73		
OH	16.4	9.31	7.1	122.1	119	3.1	13.0	13.17	−0.17
H_2O^+	230.6	233	−2.4	137.5	129.1	8.4	35.3		
O_2H	−3.4	5.0	−8.4	80.3	90	−9.7	10.86	11.53	−0.67
NO	21.1	21.6	−0.5	56.0	49.9	6.1	9.32	9.25	0.07
NO_2	−25.3	7.9	−33.2	40.4	78.6	−38.2	9.89	9.80	0.09
NH_2	29.1	41	−11.9	90.6	103	−9.4	10.53	11.40	−0.87
CHO	−4.0	−4.12	0.12	73.6	88	−14.4	9.04	9.83	−0.79
CH_3O	4.8	−0.5	5.3	107	102	5	10.81	9.2[e]	1.61
CH_3CO	−25.1	−4.5	−20.6	70.6	88	−17.4	8.17	8.05	0.12
CF	42.5	68	−25.5	79.4	83.1	−3.7	8.23	13.8	−5.57
CH_2F	−15.5	−6.6	−10.4	87.8	101	−13.2	9.8	9.4	0.4
CHF_2	−91.5	−70.2	−21.3	66.6	101	−34.4	10.11	9.45	0.66
CF_3	−168.6	−114	−54.6	49.3	106	−56.7	11.14	10.1	1.04
C_2F	71.2	66 ± 10[e]	5.2	107.2	88.7	18.5	10.12		
CN	58.8	100	−41.2	76.5	129	−52.5	10.3	14.5	−4.2
NH_3^+	203	223	−20	101.2	125.1	−23.9	21.89	23.5	−1.61
CCl	98.8	122	−23.2	83.2	94.1	−10.9	8.58	12.9	−4.32
CH_2Cl	25.7	29	−3.3	93.1	94.4	−1.3	9.55	9.32	0.23
$CHCl_2$	11.3	31	−19.7	85.7	106.1	−20.4	9.50	9.30	0.20
CCl_3	−0.8	14	−14.8	77.3	90.7	−13.4	9.56	8.78	0.78

[a] Values, unless otherwise stated, from J. L. Franklin, J. D. Dillard, H. M. Rosenstock, Y. T. Herron, K. Draxl, and F. M. Field, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, **No. 26** (1969). [b] Calculated by thermocycle using either calculated or experimental heats of formation. [c] D. F. McMillen, D. M. Golden, and S. W. Benson, *Int. J. Chem. Kinet.*, **4**, 487 (1972). [d] J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966). [e] V. I. Vedeneyco, L. V. Gurvich, V. N. Kondrat'yev, V. A. Medvedev, and Ye L. Frankevich, "Bond Energies, Ionization Potentials, and Electron Affinities", Edward Arnold, London, 1966.

$$E(\mathrm{M}) = (1/2) \sum_i \sum_j (p_{ij}{}^{\alpha} F_{ij}{}^{\alpha} + p_{ij}{}^{\beta} F_{ij}{}^{\beta} + p_{ij} H_{ij}) + E_c \tag{9}$$

where E_c represents the core-core repulsion energy term.

In order to minimize this energy with respect to the geometrical variables, the Fletcher-Powell algorithm[13] was adopted. Since the calculation of gradients and their scalar products used in this method is performed quite differently in our program compared to the original one,[7] some computational details about this subject shall be given.

If the geometry of a molecule consisting of N nuclei is represented as a $3N - 6$ dimensional vector $|x\rangle$, the energy E and the population matrices P^{α} and P^{β} can be calculated at any given point $|x\rangle$. Assuming that for small changes in geometry the bond order matrices P^{α} and P^{β} remain constant, the individual gradients can be calculated by finite differences as

$$(\partial E/\partial x_i)_{x_{k,k\neq i}} \simeq (E_i{}^+ - E_i{}^-)/2\Delta \tag{10}$$

where E^+ and E^- correspond to the geometries

$$|x\rangle_i{}^+ = (x_1, x_2, \ldots, x_i + \Delta, x_{i+1} \ldots) \tag{11}$$

and

$$|x\rangle_i{}^- = (x_1, x_2, \ldots, x_i - \Delta, x_{i+1} \ldots) \tag{12}$$

respectively.

Omitting all terms that cancel in eq 10, only contributions

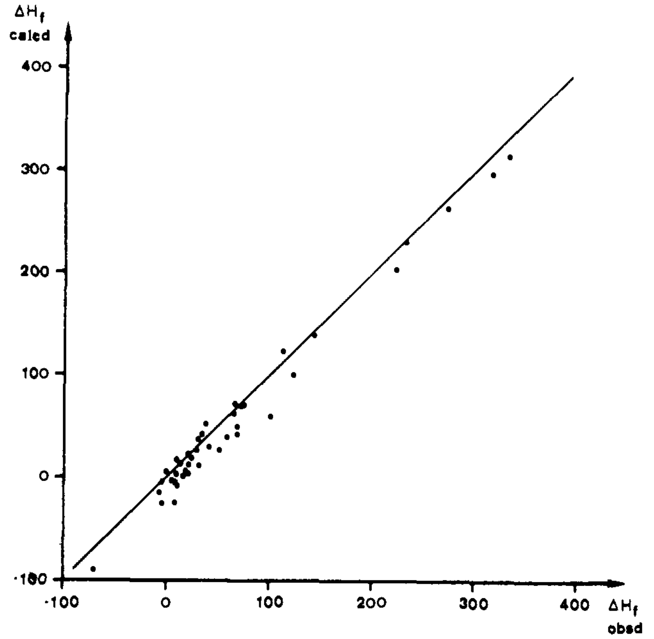

Figure 1. Plot of calculated (ΔH_f (calcd)) vs. observed heats of formation (ΔH_f (obsd)) in kcal/mol. The line shown is the theoretical line of unit slope.

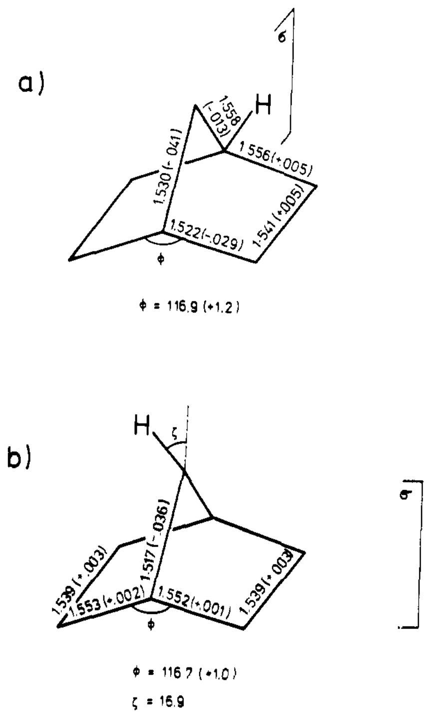

Figure 2. Predicted equilibrium structures of the 1-norbornyl (a) and the 7-norbornyl radical (b). The numbers in parentheses are the predicted deviations of the corresponding values as compared to parent norbornane. Φ denotes the dihedral angles between the planes $C^1C^2C^3C^4$ and $C^1C^4C^5C^6$. The predicted planes of symmetry (σ) are shown for both radicals.

depending on the overlap S_{ij} (E_S) and the electronic repulsions γ_{mn} (E_γ) have to be considered for the electronic energy parts. An appropriate energy partitioning is therefore given by

$$E^{\pm} = E_S{}^{\pm} + E_\gamma{}^{\pm} + E_c{}^{\pm} + \text{constant} \qquad (13)$$

Substituting eq 1-8 into eq 9 finally yields the following reduced energy terms:

$$E_S{}^{\pm} = \sum_i^{(m)<(n)} \sum_j 2B_{mn}(I_i + I_j)(p_{ij}{}^\alpha + p_{ij}{}^\beta)S_{ij}{}^{\pm} \qquad (14)$$

$$E_\gamma{}^{\pm} = \sum_{m<n}\sum (Q_mQ_n - Q_mC_n - Q_nC_m - \pi_{mn})\gamma_{mn}{}^{\pm} \qquad (15)$$

where

$$Q_m = \sum_i^{(m)} p_{ii} \qquad (16)$$

and

$$\pi_{mn} = \sum_i^{(m)}\sum_j^{(n)} (p_{ij}{}^\alpha p_{ij}{}^\alpha + p_{ij}{}^\beta p_{ij}{}^\beta) \qquad (17)$$

While the gain in computer time by using these reduced formulas was negligible, the numerical stability of the gradients has improved a lot. A further refinement has been achieved by recognizing that eq 10 can be applied to any desired search vector $|s\rangle$ directly. This way, excessive gradient calculations were avoided, since the individual components of the gradient $|g\rangle$ need not be known for its scalar product $\langle g|s\rangle$. This is especially important if the gradients need to be calculated by full SCF calculations, which seems to be necessary if configuration interaction has to be taken into account.

Results

Energies. Table I summarizes the calculated heats of formation (ΔH_f), the calculated hydrogen atom affinities (ΔH_H), and ionization potentials (I_V) of various radicals.

The calculated heats of formation are correlated with experimental values in Figure 1. All results correspond to the predicted equilibrium structure of the radicals, which was obtained in the usual manner by total geometry optimization as outlined above. The ionization potentials are estimated using Koopmans' theorem.[10] The choice of examples was taken quite randomly, although emphasis has been put on pure hydrocarbons.

Table I reveals that, with very few exceptions, all radicals are predicted too stable by an average of 10 kcal/mol as compared with experiment. This had to be expected, since the parameters adjusted for closed-shell systems already account for correlation energy, part of which is taken twice over if α and β electrons are allowed to occupy different spatial orbitals. This has been discussed in detail by Dewar et al.[8]

Recognizing this tendency, the calculated heats of formation compare reasonably well with experiment. The defects parallel those for closed-shell systems in as far as strongly hydrogen-crowded radicals are consistently too high in energy as compared to others. Note that most isomers are calculated in correct energy ordering among each other. This is especially promising in view of a possible application of MINDO/3 to intramolecular rearrangement reactions of radicals, for which experimental evidence is mostly speculative.

The mechanism of a fragmentation reaction is mainly controlled by the relative bond strengths within a molecule. The observed correct ordering of the corresponding fragments, therefore, is encouraging for this type of reaction as well.

Geometries. The strong interplay between geometry and electronic structure of molecules demands that a reliable semiempirical method not only yields quite good energies but reasonable geometries as well. The optimized structural parameters are given in Table II and compared to experiment where such data were available. As in closed shell systems, the predicted geometries compare usually quite well with experiment.

The methyl radical was calculated to be slightly pyramidal, while the isoelectronic $NH_3{}^+$ cation was found to be planar. This parallels ab initio calculations by Pople et al.[14] using the STO-3G basis set, while their calculations on the 4-31G level

Table II[h]

Radical	Point group	Calcd (obsd) geometrical variables[i]	Ref
CH	$C_{\infty v}$	CH, 1.119 (1.120)	*a*
CH_2^+	C_{2v}	CH, 1.093; HCH, 137.6	
CH_3	C_{3v}	CH, 1.091 (1.079); HCH, 117.0 (120)	*b*
CH_4^+	C_{2v}	CH^1, 1.192; CH^2, 1.095; H^1CH^1, 49.5; H^2CH^2, 123.9	
C_2H	C_s	CC, 1.201; CH, 1.080; HCC, 152.81	
$C_2H_2^+$	$D_{\infty h}$	CC, 1.258; CH, 1.082	
C_2H_3	C_s	C^1C^2, 1.291; H^1C^1, 1.106; H^2C^1, 1.098; H^3C^2, 1.083; $H^1C^1C^2$, 125.3; $H^2C^1C^2$, 123.9; $H^3C^2C^1$, 146.0	
CH_2CH_3	C_s	C^1C^2, 1.44; C^1H^1, 1.097; C^2H^3, 1.116; C^2H^4, 1.111; $H^1C^1C^2$, 122.8; $H^1C^1H^2$, 112.7; $C^1C^2H^3$, 112.4; $C^1C^2H^4$, 113.5; $H^4C^2H^5$, 106.3	
$CHCCH_2$	C_{2v}	C^1C^2, 1.38; C^2C^3, 1.22; H^1C^1, 1.095; H^3C^3, 1.071; $H^1C^1H^2$, 113.7	
CH_2CHCH_2	C_{2v}	CC, 1.379; C^1H, 1.098; C^2H, 1.112; HC^1H, 111.7; C^1C^2H, 114.6; CCC, 130.8	
c-C_3H_5	C_s	C^1C^2, 1.462; C^2C^2, 1.507; C^1H, 1.09; C^2H, 1.107; HC^2H, 108.5; $C^2C^1C^2$, 62.1	
$CH_3C{=}CH_2$	C_s	C^1C^2, 1.425; C^2C^3, 1.296; C^1H, 1.11; C^3H, 1.10; $C^1C^2C^3$, 166; HC^1H, 106; HC^3H, 110.5	
n-C_3H_7	C_s	C^1C^2, 1.494; C^2C^3, 1.454; C^1H, 1.11; C^2H, 1.124; C^3H, 1.096; $C^1C^2C^3$, 121.3; HC^1H, 105.5; HC^2H, 101.4; HC^3H, 112.8	
i-C_3H_7	C_{2v}	C^1C^2, 1.456; C^1H, 1.113; C^2H, 1.108; $C^1C^2C^3$, 131.1; HC^1H, 105.5	
c-C_4H_7	C_{2v}	C^1C^2, 1.487; C^2C^3, 1.532; $C^2C^1C^2$, 94.3; $C^1C^2C^3$, 87.5; $C^2C^3C^2$, 90.7; HC^2H, 99.2; HC^3H, 117.9	
$(CH_2)_2CCH_3$	C_s	C^1C^2, 1.496; C^2C^3, 1.398; C^1H, 1.11; C^2H, 1.098; $C^3C^2C^3$,119.7; HC^1H, 105.2; HC^3H, 111.0	
n-C_4H_9	C_1	C^1C^2, 1.455; C^2C^3, 1.513; C^3C^4, 1.495; C^1H, 1.096; C^2H, 1.124; C^3H, 1.121; C^4H, 1.11; HC^1H, 112.7; HC^2H, 101.4; HC^3H, 102.2; HC^4H, 105.4	
i-C_4H_9	C_1	C^1C^2, 1.474; C^2C^3, 1.515; C^1H, 1.096; C^2H, 1.135; C^3H, 1.111; HC^1H, 112.75; C^1C^2H, 103.45, HC^3H, 105.0	
s-C_4H_9	C_1	C^1C^{en}(methylene), 1.474; C^1C^m(methyl), 1.457; $C^{en}C^e$(ethyl), 1.495; C^1H, 1.107; $C^{en}H$, 1.12; C^mH, 1.111; C^3H, 1.111; $C^mC^1C^2$, 129.6; $C^eC^2C^1$, 120.6; HC^mH, 105.7; $HC^{en}H$, 101.9; HC^eH, 105.6	
t-C_4H_9	C_3	CC, 1.479; CH, 1.112; CCC, 120; HCH, 105.2	
c-C_5H_9	C_{2v}	C^1C^2, 1.483; C^2C^3, 1.525; C^3C^3, 1.530; C^1H, 1.10; C^2H, 1.118; C^3H, 1.118; $C^2C^1C^2$, 112.3; $C^3C^2C^1$, 106.0; $C^3C^3C^2$, 107.8; HC^2H, 102.4; HC^3H, 102.9	
c-C_6H_{11}	C_s	C^1C^2, 1.478; C^2C^3, 1.520; C^3C^4, 1.520; C^1H, 1.10; C^2H, 1.12; C^3H, 1.12; C^4H, 1.12; HC^2H, 101.65; HC^3H, 102.0; HC^4H, 102.0	
Phenyl	C_{2v}	C^1C^2, 1.386; C^2C^3, 1.411; C^2H, 1.102; C^3H, 1.105; C^4H, 1.105; $C^2C^1C^2$, 127.5; $C^3C^2C^1$, 115.6; $C^3C^4C^3$, 120.7	
Benzyl	C_{2v}	C^1C^2, 1.455; C^2C^3, 1.401; C^3C^4, 1.415; C^1C^7, 1.401; C^2H, 1.106; C^3H, 1.105; C^4H, 1.104; C^7H, 1.098; $C^2C^1C^2$, 114.4; $C^3C^2C^1$, 122.7; $C^3C^4C^3$, 119.4; HC^7H, 111.4	
Phenoxy	C_{2v}	C^1O, 1.216; C^1C^2, 1.489; C^2C^3, 1.388; C^3C^4, 1.425; C^2H, 1.105; C^3H, 1.106; C^4H, 1.104; $C^2C^1C^2$, 115.2; $C^1C^2C^3$, 121.5; $C^2C^3C^4$, 120.8; $C^3C^4C^3$, 120.2	
1-Norbornyl	C_s	See Figure 2	
7-Norbornyl ·	C_s	See Figure 2	
OH	$C_{\infty v}$	OH, 0.947 (0.971)	*a*
H_2O^+	C_{2v}	OH, 0.974; HOH, 108.7	
HO_2	C_s	OH, 0.976 (0.958); OO, 1.278 (1.30); HOO, 111.4 (105)	*c*
NO	$C_{\infty v}$	NO, 1.164 (1.151)	*a*
NO_2	C_{2v}	NO, 1.185 (1.197); ONO, 153.73 (134.25)	*d*
NH_2	C_{2v}	NH, 1.035 (1.024); HNH, 102.5 (103)	*d*
CHO	C_s	CH, 1.136 (1.110); CO, 1.154 (1.171); HCO, 136.6 (127.4)	*e*
CH_3O	C_{3v}	CO, 1.291; CH, 1.125; HCH, 105.5	
CH_3CO	C_s	CC, 1.458; CO, 1.169; CH, 1.111; OCC, 141.1; HCH, 106	
CF	$C_{\infty v}$	CF, 1.256 (1.267)	*d*
CH_2F	C_s	CH, 1.102; CF, 1.318; HCH, 113.1; HCF,115.4	
CHF_2	C_{2v}	CH, 1.114; CF, 1.284; FCF, 138.7	
CF_3	D_{3h}	CF, 1.288 (1.33); FCF, 120 (112)	*d*
C_2F	C_s	CC, 1.229; CF, 1.316; CCF, 149.8	
CN	$C_{\infty v}$	CN, 1.132 (1.172)	*a*
NH_3^+	D_{3h}	NH, 1.013 (1.07); HNH, 120 (120)	*g*
CCl	$C_{\infty v}$	CCl, 1.641 (1.642)	*d*
CH_2Cl	C_s	CH, 1.095; CCl, 1.698; HCH, 115.0; HCCl, 115.3	
$CHCl_2$	C_s	CH, 1.101; CCl, 1.704; HCCl, 111.4; ClCCl, 123.3	
CCl_3	C_{3v}	CCl, 1.716 (1.74); ClCCl, 117.3 (120)	*d*

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Table III

Radical	$\langle S^2\rangle_{SD}$	$\langle S^2\rangle_{AA}$	Proton	a_{SD}[a]	a_{AA}[b]	a_{expt}[c]
CH_3	0.760	0.750		−16.73	−2.38	−23.04
C_2H	0.809	0.752		50.33	52.16	16.16
C_2H_3	0.820	0.752	α	−1.23	14.54	16.0
			β trans	19.92	16.42	34.0
			β cis	67.76	63.83	68.0
C_2H_5	0.767	0.750	α	−24.08	−9.97	(−)22.38
			β	20.37	18.31	(−)26.87
$CHCCH_2$	0.852	0.756	−CH	−17.34	−7.4	(−)12.80[d]
			−CH_2	−27.22	−11.75	(−)18.90[d]
Allyl	0.904	0.756	α	−19.40	−7.95	(−)13.93[e]
			α′	−20.97	−8.61	(−)14.83[e]
			β	11.51	4.71	4.06[e]
c-C_3H_5	0.764	0.750	α	−7.11	5.28	6.51[f]
			β	14.90	14.11	23.42[f]
n-C_3H_7	0.768	0.750	α	−25.46	−10.96	(−)22.08
			β	29.76	26.58	33.2
			γ	−1.47	−0.66	(−)0.38
i-C_3H_7	0.768	0.750	α	−25.54	−11.63	(−)22.11
			β	17.99	15.98	24.68
c-C_4H_7	0.771	0.750	α	−21.96	−9.95	(−)21.20
			β	23.92	21.15	36.66
			γ	−2.01	−0.80	(−)1.12
i-C_4H_9	0.769	0.750	α	−26.14	−11.87	(−)21.8
			β(CH_3)	18.0	16.0	24.5
			β(CH_2)	21.96	19.55	27.9
			γ(CH_3)	−1.27	−0.49	
s-C_4H_9	0.769	0.750	α	−26.6	−12.1	(−)22.0
			β	33.9	30.0	35.1
			γ	−1.16	−0.37	
t-C_4H_9	0.768	0.750		15.29	13.58	22.72
c-C_5H_9	0.769	0.750	α	−23.51	−9.93	(−)21.48
			β	23.72	21.12	35.16
			γ	−1.23	−0.53	(−)0.53
c-C_6H_{11}	0.770	0.750	α	−25.27	−11.4	(−)21.15
			β	24.78	22.08	45.96
			γ	−1.58	−0.69	(−)0.71
			δ	0.36	0.19	
Phenyl	1.021	0.809	o	10.84	6.48	18.10[f]
			m	0.64	4.43	6.40[f]
			p	12.05	5.54	3.0[f]
Benzyl	1.172	0.909	-CH_2	−21.75	−6.76	(−)16.35[e]
			o	−14.0	−4.32	(−)5.14[e]
			m	11.0	3.39	1.75[e]
			p	−13.72	−4.24	(−)6.14[e]
Phenoxy	1.066	0.825	o	−16.0	−5.62	(−)6.60[e]
			m	10.91	3.83	1.96[e]
			p	−17.30	−6.08	(−)10.4[e]
HCO	0.758	0.750		119.8	145.1	137.0
CH_3CO	0.755	0.750		8.72	9.5	5.1

[a] Calculated as $a_{SD} = 394\zeta_{SD}$, where ζ_{SD} is the single determinant spin density. [b] Calculated as $a_{AA} = 540\zeta_{AA}$, where ζ_{AA} is the annihilated atomic spin density. [c] M. Bersohn and J. C. Baird, "An Introduction to Electron Paramagnetic Resonance", W. A. Benjamin, New York, N.Y., 1966, and references cited therein. [d] See ref 20. [e] Reference 12c. [f] Reference 1.

predicts both radicals to be planar. Experimental evidence[15] favors a planar structure of CH_3. Although MINDO/3 is by far superior to the mentioned ab initio method in predicting inversion barriers of AH_3 systems,[16] our result is definitely not conclusive: it is on line with the general trend of MINDO/3 to underestimate HCH bond angles in methyl groups.[5] In addition, the calculated inversion barrier of CH_3 is only 0.7 kcal/mol.

While the formyl,[19] vinyl,[20] and acetyl[21] radicals are known to be bent and are correctly predicted so, the ethynyl radical is linear[22] or nearly so.[23] MINDO/3 yields a slightly bent radical, although the inversion barrier again is less than 1 kcal/mol. This is a surprising result considering the fact that the isoelectronic cations HCN^+ and $C_2H_2^+$ are calculated to be linear. Note that the predicted C–C bond length in C_2H is only 0.01 Å longer than the one calculated for acetylene, indicating a real triple C–C bond in spite of the nonlinearity of the radical.

Spin Densities. To conclude the brief discussion of obtained results, the calculated hydrogen spin densities shall be compared with EPR coupling constants. This comparison was made using the same method as described by Pople et al.[24] Two independent least-squares analyses were made for the spin densities before (ζ_{SD}) and after (ζ_{AA}) annihilation of higher spin components. The spin projection was performed using the approximate technique described by Amos and Snyder.[25] Table III shows the final results for a number of radicals, together with the expectation values of the S^2 operator before ($\langle S^2\rangle_{SD}$) and after ($\langle S^2\rangle_{AA}$) annihilation. It turned out that spin projection did not improve the resulting correlation coefficient, which for both sets of data was 0.95. However, the theoretical slope of $K = 506$ G was much closer approached by the annihilated spin densities.[26] Furthermore, the relative coupling constants for the various hydrogen atoms within any specific radical (e.g., the assignments of the EPR spectra) are much better reproduced by the annihilated correlation.

The drastic changes of spin densities with geometry is very nicely demonstrated by the phenoxy radical, where the "assumed" geometry yields the wrong ordering, while the optimized structure correctly predicts a_{H} (ortho) $< a_{\mathrm{H}}$ (para).

The strong influence of solvent upon hyperfine interaction is well known and has been tackled by various theoretical models.[27] For uncharged, unpolar species as those given in Table III this effect can safely be considered to be negligible.

Conclusions

The reasonable accuracy with which energies, geometries, and spin distributions of radicals are calculated by the unrestricted MINDO/3 open-shell method shows that this treatment is suitable as a predictive tool in radical chemistry. Although for the reason outlined above the radicals are consistently predicted too stable, this method is superior to the half-electron method mainly because of geometry optimization reasons.

Computer Programs. A deck of the MINDO/3-UHF (Unrestricted Hartree Fock) program, including geometry optimization and spin projection, will be deposited with the Quantum Chemistry Program Exchange.

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Extent of Localization of Orbitals in Loges and the Electron Pair Concept

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Abstract: The extent of pair localization in a molecule is discussed in terms of orbitals. It is argued that orbitals may be localized in loges to a degree which is more compatible with the electron pair concept than is suggested by the values of $|F(\Omega,\Omega)/\bar{N}(\Omega)|$, where $|F(\Omega,\Omega)/\bar{N}(\Omega)|$ is the fractional localization of electrons in loge Ω, $\bar{N}(\Omega)$ is the average number of electrons in Ω, and $F(\Omega,\Omega)$ is equal to the fluctuation in the population of Ω minus $\bar{N}(\Omega)$. Consider an N-electron closed shell system described by a Hartree-Fock wave function consisting of $N/2$ space orbitals. Let μ_1 be that orbital in the Hartree-Fock space which has the largest fraction of its charge density within the loge Ω. This fraction is equal to $\langle\mu_1|\mu_1\rangle_\Omega$, where $\langle\mu_1/\mu_1\rangle_\Omega$ is the overlap of μ_1 with itself over the region Ω. In addition, if $\bar{N}(\Omega) = 2$, then $\langle\mu_1|\mu_1\rangle_\Omega$ also turns out to be the fractional contribution of μ_1 to the average number of electrons in Ω. Thus $\langle\mu_1|\mu_1\rangle_\Omega$ should serve as a reasonable assessment of the extent of localization of μ_1 within Ω. The value of $\langle\mu_1|\mu_1\rangle_\Omega$ may be significantly larger than the value of $|F(\Omega,\Omega)/\bar{N}(\Omega)|$. For example, in the CH bond loge of CH_4, $\langle\mu_1|\mu_1\rangle_\Omega = 0.82$ while $|F(\Omega,\Omega)/\bar{N}(\Omega)| = 0.69$. Furthermore, it is shown that $\langle\mu_1|\mu_1\rangle_\Omega$ is often approximately equal to $|F(\Omega,\Omega)/\bar{N}(\Omega)|^{1/2}$.

Introduction

The electron pair concept has been a central feature of chemistry. It is therefore pertinent that the recent important work of Bader and Stephens[1a] implies that the model of spatially localized pairs is not quite suitable for many molecules. For instance, the model was argued to be of only borderline applicability in CH_4. With this in mind, it is the purpose of this article to discuss the question of pair localization in terms of the maximum extent that an orbital may be localized within a loge.[2]