

Thermodynamical Properties and Structural Data of Radicals Calculated by MNDO-UHF

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The MNDO-UHF method has been applied to a large number of organic and inorganic radical species. The obtained results demonstrate that thermodynamical data as well as their equilibrium structures are in reasonable agreement with experimental findings.

INTRODUCTION

Within the last fifteen years, semiempirical molecular orbital calculations have developed from the stage of a mainly educational trimming into the powerful tool of "experimental computer chemistry."¹ Among the various available methods, calculations of INDO- and MINDO-type for a long time seemed to represent the optimal grade of sophistication, because the next necessary step to the NDDO level of approximation calls for the calculation of a relatively large number of different two-center integrals.

Dewar and Thiel² have succeeded in approximating these integrals by sums of classical multipole-multipole interactions and to define their numerical values using no additional parameters. The resulting MNDO framework proved to be superior to any of the MINDO schemes, especially for systems including heteroatoms, where lone pairs have a large influence on the electronic structure and thus determine the geometry and configuration of the corresponding molecules.

Some time ago, we extended the MINDO/3 method³ into an unrestricted Hartree-Fock version⁴ and applied it very successfully to the study of the electronic structure of radicals.⁵ From our results we concluded that MINDO/3 is just as reliable for such species as for "normal" closed-shell molecules, although no radicals were ever accounted for in the parametrization procedure. However, some of the typical MINDO failures—which could be traced to the insufficiencies of the INDO approximation—again showed up in the UHF treatment. Since the electronic structures of σ -type radicals resemble those of molecules con-

taining electron lone pairs, it was therefore evidently necessary to look for more success in the MNDO framework, where such configurations are treated more adequate.

We adopted the necessary routines of the MNDO program⁶ to our UHF version of MINDO/3 (MOPN⁷) and applied the program to a large number of doublet systems. In this work, we wish to present the obtained results and conclusions.

THEORY AND COMPUTER PROGRAM

The basic approximations of the closed-shell MNDO treatment have been outlined in detail by Dewar and Thiel.² The extension to an unrestricted Hartree-Fock version leads to changes of the Fock matrix elements for the electron-electron repulsion terms, because α - and β -spin distributions in this framework are not identical.

Using the same symbols and formalism as in ref. 5, the corresponding Fock matrix elements take the following form:

$$F_{ii}^{\alpha}(m) = H_{ii} + p_{ii}^{\beta}g_{ii} + \sum_{k \neq i}^{(m)} (p_{kk}g_{ik} - p_{kk}^{\alpha}h_{ik}) + \sum_{n \neq m}^{(n)} \sum_k^{(n)} \sum_l^{(n)} p_{kl}(ii|kl) \quad (1)$$

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

$$F_{ij}^{\alpha}(m,n) = H_{ij} - \sum_k^{(m)} \sum_l^{(n)} p_{kl}^{\alpha}(ik|jl) \quad (3)$$

where

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

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

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

$$H_{ii} = U_{ii} - \sum_{n \neq m} C_n(ii|ss) \quad (7)$$

and

$$H_{ij} = \beta_{ij} = S_{ij}(I_i + I_j)(\beta_n + \beta_m) \quad (8)$$

The parameters optimized for closed-shell molecules² were adopted with no change.

Because the number of necessary two-center integrals becomes quite large even for systems of moderate size, they have to be stored on disk files. This made it prohibitive to calculate gradients using the same energy partitioning scheme as in MOPN,⁷ and we therefore returned to the standard way⁸ of calculating these values.

The program includes an improved version of the symmetry analyses package which calculates the point group of the molecule, irreducible representations of molecular orbitals, and molecular vibrations. Furthermore, an energy-partitioning routine has been added to the FORTRAN IV deck which will be available from the Quantum Chemistry Program Exchange.

All calculations were performed on an IBM 370/168 computer.

RESULTS AND DISCUSSION

Thermodynamical Properties

Table I summarizes the heats of formation, hydrogen atom affinities, ionization potentials, and standard entropies of the calculated radicals.

The hydrogen atom affinities were calculated by thermocycle using either the predicted heats of formation ($\Delta H_{\text{H}}^{\text{calc}}$) or the experimentally determined heats of formation ($\Delta H_{\text{H}}^{\text{exp}}$) of *all* species involved in the theoretical reaction



The tabulated ionization potentials are the negative orbital energies of the highest occupied molecular orbital, assuming the validity of Koopmans' theorem.⁹

Evidently with very few exceptions, most heats of formation are too low by an average of 50 kJ/mol. This has already been anticipated in

MINDO/3-UHF and is well understood: The use of different spatial orbitals for α - and β -spin electrons allows for additional correlation. This energy, however, has already been accounted for in the choice of parameters. Hence, it is taken twice over and leads to the observed overestimation of stability.

The resulting shift of the energy scale towards lower values is no serious handicap and does not affect the "chemical reliability" of the method, because relative energy values only determine rate constants and chemical equilibrium. Due care has to be taken in calculations of recombination or disproportionation reactions where appropriate corrections have to be considered.

On the other hand, the obtained results reveal that the relative stabilities of isomer radicals are in most cases predicted correctly. However, there are some distinct exceptions which do not fit in this simple picture: The ethynyl radical (C_2H), cyano (CN), and fluoroethynyl radical (C_2F) are predicted as too unstable by more than 100 kJ/mol. All of these species contain a triple bond. Surprisingly, a corresponding misfit of the heats of formation calculated for their parent closed-shell analogs (HCN, etc.) is absent,² while similar errors are found for the corresponding anions (CN^- , etc.). This reflects in a vast overestimation of the corresponding hydrogen atom affinities.

Apart from these findings, the reliability of calculated heats of formation of radicals is about the same as for closed-shell species,² the mean-square deviation from the theoretical line with unit slope through the origin being 80 kJ/mol.

This pleasing result confirms that the parameters optimized by Dewar and Thiel can be used for open-shell calculations as well: an application which was not considered in their original parametrization.

Focusing on ionization potentials, the Koopmans values⁹ prove to be generally too high. This is on line with the mentioned tendency to overestimate the stability of doublet systems, since the energy difference between the radical and its closed-shell cation (i.e., in most cases the first ionization potential) is expected to be overestimated as well. It should be noted that the general fit of calculated ionization potentials is not as good as for closed-shell molecules. The same observation was made comparing MINDO/3-UHF⁵ values with experimental ionization potentials.

To conclude the discussion of energetic aspects, we wish to comment on the standard entropies S_{298}° given in the last row of Table I.

Table I. Heats of formation (ΔH_f), hydrogen atom affinities (ΔH_H), ionization potentials (I_v), and standard entropies (S_{298}°) of radicals as calculated by UHF-MNDO (calc) and compared with available experimental values (exp). ΔH_f and ΔH_H in kJ/mol, I_v in eV, and S_{298}° in J/K mol.



Radical	ΔH_f			ΔH_H			I_v			S_{298}°		
	calc	exp	err	calc	exp	err	calc	exp	err	calc	exp	err
CH	600	596a	4	368	422	-54	9.40	11.13a	-1.73	171	183f	-12
CH ₂ ⁺	1251	1393a	-142	449	523	-74	18.86			189		
CH ₃	103	139a	-36	371	432	-61	9.70	9.84b	-0.14	198	194f	4
CH ₄ ⁺	1148	1146a	2	337	435	-98	20.23			219		
C ₂ H	623	469a	154	601	459	142	11.16	11.30c	-0.14	200	241f	-41
C ₂ H ₂ ⁺	1265	1326a	-61	372	431	-59	18.58			204		
C ₂ H ₃	246	299b	-53	400	465	-65	9.46	9.45a	0.01	236		
C ₂ H ₄ ⁺	995	1059a	-64	293	360	-67	18.10			229		
C ₂ H ₅	44	105a	-61	344	407	-63	9.48	8.51b	0.97	244		
CHCCH ₂	280	314a	-34	327	346	-19	9.09	8.34a	0.75	248		
CH ₂ CHCH ₂	106	183b	-77	303	380	-77	9.06	8.13d	0.93	257		
c-C ₃ H ₅	212	278b	-66	383	443	-60	9.54	8.05a	0.98	261		
CH ₃ CCH ₂	169	243a	-74	366	440	-74	9.25			271		
n-C ₃ H ₇	22	93a	-71	344	414	-70	9.47	8.10a	1.37	274		
i-C ₃ H ₇	-6	70a	-76	316	392	-76	9.34	7.69b	1.65	277		
(CH ₂) ₂ CCH ₃	145	88a	-57	346	279	67	9.34	8.03a	1.31	288		
c-C ₄ H ₇	81	214c	-133	349	403	-55	9.37	7.93a	1.44	269		
n-C ₄ H ₉	3	77a	-74	345	423	-77	9.47	8.64a	0.83	302		
s-C ₄ H ₉	-27	37a	-64	315	382	-67	9.32	7.93a	1.39	304		
1-C ₄ H ₉	12	53a	-41	342	407	-65	9.49	8.35a	1.14	296		
t-C ₄ H ₉	-44	19a	-63	286	372	-86	9.23	6.92b	2.31	295		
c-C ₅ H ₉	-23	92d	-115	323	387	-64	9.31	7.79a	1.52	297		
c-C ₆ H ₁₁	-48	50d	-98	316	392	-76	9.30	7.66a	1.64	315		
	138			278			8.84			305		
	142			277			8.85			310		
c-C ₃ H ₃	425	440b	-15	358	381	-23	7.99	5.80a	2.19	247		
c-C ₅ H ₅	210	264b	-54	294	349	-55	8.96	8.69a	0.23	274		
c-C ₇ H ₇	166	289b	-123	244	323	-79	7.93	6.28e	1.65			
Phenyl	288	301a	-13	418	436	-19	9.85	9.20a	0.65	288		
Phenoxy	-20	48b	-68	301	363	-62	9.69	8.84a	0.85	309		
Benzyl	133	201b	-68	294	369	-75	8.83	7.20d	1.07	313		
1-Norbornyl	134			395			9.59			309		
7-Norbornyl	78			339			9.34			305		
ω -Butenyl	125			342			9.46			294		
ω -Pentenyl	105			344			9.47			319		
OH	1	39a	-38	474	499	-25	12.26	13.17a	-0.91	172	184f	-12
H ₂ O ⁺	877	975a	-98	534	611	-77	25.02			194		
O ₂ H	-47	21a	-68	331	375	-44	11.60	11.53a	0.07	226	227f	-1
CHO	-6	-17a	11	350	310	40	8.95	9.83a	-0.88	221	225f	-4
CHO ₂	-147			459			11.86			245		
CH ₃ O	-24	-2a	-22	434	417	17	11.24	9.20e	2.04	226		
CH ₃ CO	-68	-19a	-49	327	365	-38	8.73			261		
CH ₃ CO ₂	-184			457			11.66			282		
NH ₂	153	171a	-18	397	436	-38	12.13	11.40a	0.73	194	195f	-1
NH ₃ ⁺	926	933a	-7	455	502	-47	22.16	23.50a	-1.34	198		
CN	527	418a	109	599	501	98	13.65	14.50a	-0.90	196	202f	-6
NO	-2	90a	-92	201	209	-8	10.22	9.25a	0.97	199	210f	-11
NO ₂	-26	33a	-59	362	330	-32	11.97	9.80a	2.17	239	239f	0
Succinimidyl	-160			426			10.91			325		
CF	160	284a	-124	288	377	-89	9.26	13.80a	-4.54	201	213f	-12
CH ₂ F	-144	-28a	-116	328	424	-96	9.67	9.40a	0.27	228		

Table I (continued)

CHF ₂	-374	-294a	-80	311	377	-65	10.00	9.45a	0.55	258		
CF ₃	-581	-477a	-104	323	437	-114	11.47	10.10a	1.37	264	265f	-1
C ₂ F	451	276e	175	606	369	237	10.49			243		
C ₂ F ⁺	257	326a	-69	282			17.88			312		
CCl	445	510a	-65	325	394	-69	9.84	12.90a	-3.06	214	224f	-10
CH ₂ Cl	45	121a	-76	358	425	-67	9.98	9.32a	0.66	239		
CHCl ₂	8	130a	-122	344	444	-100	10.18	9.30a	0.88	274		
CCl ₃	-9	59a	-68	331	379	-48	10.33	8.78a	1.55	306	297f	9
C ₂ Cl ⁺	935	925a	10	239			16.59			355		
N ₃	406	414g	-8	319	333	-14	10.28			222	226g	-4
NCO	131	159g	-28	395	494	-99	11.29			233	232g	1

^a 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 D. J. Defrees, R. T. McIver, and W. J. Hehre, *J. Am. Chem. Soc.*, **102**, 3334 (1980).

^c D. F. McMillen, D. M. Golden, and S. W. Benson, *Int. J. Chem. Kinet.*, **4**, 487 (1972).

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^e V. I. Vedeneyco, L. V. Gurvich, V. N. Kondrat'yev, V. A. Medwedev, and Y. L. Frankevich, *Bond Energies, Ionisation Potentials and Electron Affinities*, Edward & Arnold, London, 1966.

^f D. R. Stull and H. Prophet, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, No. 37 (1971).

^g M. W. Chase, J. L. Curnutt, A. T. Hu, H. Prophet, A. N. Syverud, and L. C. Walker, *J. Phys. Chem. Ref. Data*, **3**, 311 (1974).

The theoretical values ($S_{298}^{\circ, \text{calc}}$) were obtained by using the formalism described in ref. 10. In statistical thermodynamics,¹¹ the entropy of a system is calculated as the sum of five major contributions as

$$S_{298}^{\circ} = S_{298}^{\text{trans}} + S_{298}^{\text{rot}} + S_{298}^{\text{vib-rot}} + S_{298}^{\text{vib}} + S_{298}^{\text{el}} \quad (10)$$

in the order of decreasing magnitude. From these contributions, the translational term (S_{298}^{trans}) and the rotational term (S_{298}^{rot}) are easily calculated. Neglecting all contributions of electronically excited states (which are normally very small), the electronic contribution (S_{298}^{el}) reduces to the single, constant term of 5.8 J/K mol for a doublet system. The only difficult parts to calculate are the contributions of internal rotors ($S_{298}^{\text{vib-rot}}$) and molecular vibrations (S_{298}^{vib}). As outlined in ref. 10, the force constants and vibrational frequencies are obtained by calculating the second derivatives of the energy with respect to the mass-weighted Cartesian coordinates. In this simplified picture, the contributions of internal rotors are replaced by contributions of vibrations of very low vibrational frequencies, typically in the range of 20–100 cm⁻¹. Even considering the fact that the translational part makes up for about one-half of the standard entropy, the obtained results are in excellent agreement with the experimental values, only one (the ethynyl radical) deviating more than ten international entropy units (Gibbs/mol = cal/K mol).

As anticipated earlier,¹⁰ the good prediction of standard entropies can serve as a hint that the optimized geometries (and thus the main moments of inertia) are consistent with experiment.

Geometries

All geometrical variables of the calculated radicals were fully optimized using the Fletcher Powell algorithm.¹² The resulting structures are summarized in Table II and compared with experimental values. Unfortunately, such experimental experimental data are sparse and reliable *ab initio* results for larger systems not yet available.

Nevertheless, the given structural parameters clearly show that some obvious failures of MINDO/3–UHF⁵ have been corrected by the use of the MNDO framework: MNDO correctly predicts the methyl radical as well as the trichloromethyl radical to be planar, while the trifluoromethyl radical is pyramidal and correctly predicted to be so. In all these cases, the MINDO/3–UHF prediction failed to reproduce the experimental data.

It should be kept in mind that the correct prediction of the corresponding bond angles is very important for the following reason: The hybridization of the radical site seems to have a big influence on the selectivity and reactivity of alkyl radicals¹³ and predictions made in this view must

Table II. Calculated symmetries and structures of radicals. Bond lengths in angstroms, angles in degrees.

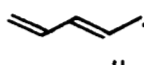
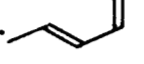



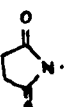
CH	$C_{\infty v}$	CH 1.097 (1.120);	a)
CH_2^+	C_{2v}	CH 1.070, HCH 165;	
CH_3	D_{3h}	CH 1.078 (1.079); HCH 120 (120);	b)
CH_4^+	C_{2v}	CH ¹ 1.204, CH ² 1.094; H ¹ CH ¹ 62, H ² CH ² 117;	
C_2H	$C_{\infty v}$	CC 1.193, CH 1.053;	
$C_2H_2^+$	$D_{\infty h}$	CC 1.267, CH 1.066;	
C_2H_3	C_s	C ¹ C ² 1.308, H ¹ C ¹ 1.092, H ² C ¹ 1.091, H ³ C ² 1.049; H ¹ C ¹ C ² 123, H ² C ¹ C ² 123, H ³ C ² C ¹ 171;	
$C_2H_4^+$	D_2	CC 1.421, CH 1.094; CCH 122, HCH 116; HCCH 26;	
CH_2CH_3	C_s	C ¹ C ² 1.475, C ¹ H ¹ 1.082, C ² H ³ 1.113, C ² H ⁴ 1.110; H ¹ C ¹ C ² 121, H ¹ C ¹ H ² 117, C ¹ C ² H ³ 112, C ¹ C ² H ⁴ 110, H ⁴ C ² H ⁵ 108;	
CHCCH ₂	C_{2v}	C ¹ C ² 1.380, C ² C ³ 1.210, H ¹ C ¹ 1.085, H ³ C ³ 1.050; H ¹ C ¹ H ² 117;	
CH ₂ CHCH ₂	C_{2v}	CC 1.397, C ¹ H 1.085, C ² H 1.096; HC ¹ H 115, C ¹ C ² H 117, CCC 126;	
c-C ₃ H ₅	C_s	C ¹ C ² 1.478, C ² C ² 1.547, C ¹ H 1.059, C ² H 1.097; H C ² H 111, C ² C ¹ C ² 63; δ 177 c);	
CH ₃ CCH ₂	C_s	C ¹ C ² 1.434, C ² C ³ 1.309, C ¹ H 1.112, C ³ H 1.091; C ¹ C ² C ³ 177, HC ¹ H 108, HC ³ H 114;	
n-C ₃ H ₇	C_s	C ¹ C ² 1.530, C ² C ³ 1.483, C ¹ H 1.109, C ² H 1.118, C ³ H 1.082; C ¹ C ² C ³ 116, HC ¹ H 108, HC ² H 106, HC ³ H 117;	
i-C ₃ H ₇	C_s	C ¹ C ² 1.483, C ¹ H 1.110, C ² H 1.089; C ¹ C ² C ³ 125, HC ¹ H 108;	
(CH ₂) ₂ CCH ₂	C_s	C ¹ C ² 1.482, C ¹ C ³ 1.451, C ² C ² 1.543, C ² H ¹ 1.097, C ³ H ² 1.110, C ³ H ³ 1.113; C ² C ¹ C ² 63, H ¹ C ² H ¹ 111, H ² C ³ H ³ 108, H ² C ³ H ² 108;	
c-C ₄ H ₇	C_{2v}	C ¹ C ² 1.501, C ² C ³ 1.558, C ¹ H 1.070, C ² H 1.106, C ³ H 1.104; C ² C ¹ C ² 94, C ¹ C ² C ³ 88, C ² C ³ C ² 90, HC ² H 108, HC ³ H 108;	
n-C ₄ H ₉	C_s	C ¹ C ² 1.484, C ² C ³ 1.540, C ³ C ⁴ 1.531, C ¹ H 1.082, C ² H 1.117, C ³ H 1.114, C ⁴ H 1.109; HC ¹ H 117, HC ² H 106, HC ³ H 106, HC ⁴ H 108;	
s-C ₄ H ₉	C_s	C ¹ C ^{en} (methylene) 1.490, C ¹ C ^m (methyl) 1.484, C ^{en} C ^e (ethyl) 1.531, C ¹ H 1.088, C ^{en} H 1.117, C ^m H 1.111, C ^e H 1.109; C ^m C ¹ C ^{en} 124, C ^e C ^{en} C ¹ 115, HC ^m H 108, HC ^{en} H 106, HC ^e H 108;	
i-C ₄ H ₉	C_s	C ¹ C ² 1.493, C ² C ³ 1.543, C ¹ H 1.082, C ² H 1.122, C ³ H 1.109; HC ¹ H 117, C ¹ C ² H 108, HC ³ H 108, C ³ C ² C ³ 113, C ³ C ² H 106;	
t-C ₄ H ₉	C_{3h}	CC 1.494, CH ¹ 1.111, CH ² 1.109; CCC 120, H ¹ CH ¹ 108, H ¹ CH ² 107;	
c-C ₅ H ₉	C_s	C ¹ C ² 1.493, C ² C ³ 1.547, C ³ C ³ 1.547, C ¹ H 1.080, C ² H 1.112, C ³ H 1.110; C ² C ¹ C ² 113, C ³ C ² C ¹ 106, C ³ C ³ C ² 108, HC ² H 106, HC ³ H 106; δ 177 d);	
c-C ₆ H ₁₁	C_s	C ¹ C ² 1.490, C ² C ³ 1.541, C ³ C ⁴ 1.533, C ¹ H 1.086, C ² H 1.116, C ³ H 1.114, C ⁴ H 1.114; HC ² H 106, HC ³ H 106, HC ⁴ H 106, C ² C ¹ H 118;	
	C_{2v}	C ¹ C ² 1.425, C ² C ³ 1.384, C ¹ H 1.094, C ² H 1.096, C ³ H 1.086; C ² C ¹ C ² 125, C ³ C ² C ¹ 125, C ¹ C ² H 118, HC ³ H 115;	
	C_s	C ¹ C ² 1.385, C ² C ³ 1.425, C ³ C ⁴ 1.425, C ⁴ C ⁵ 1.383, C ¹ H 1.086, C ² H 1.095, C ³ H 1.095, C ⁴ H 1.098, C ⁵ H 1.086; C ¹ C ² C ³ 125, C ² C ³ C ⁴ 128, C ³ C ⁴ C ⁵ 129, HC ¹ H 115, C ¹ C ² H 117, C ² C ³ H 117, C ³ C ⁴ H 116, HC ⁵ H 114;	
	C_{2v}	C ¹ C ² 1.394, C ² C ² 1.477, C ¹ H 1.065, C ² H 1.057; C ² C ¹ C ² 64, C ¹ C ² H 152;	
	C_{2v}	C ¹ C ² 1.446, C ² C ³ 1.395, C ³ C ³ 1.496, C ¹ H 1.080, C ² H 1.081, C ³ H 1.079; C ² C ¹ C ² 108, C ¹ C ² C ³ 108, C ¹ C ² H 125, C ² C ³ H 128;	
	C_{2v}	C ¹ C ² 1.407, C ² C ³ 1.433, C ³ C ⁴ 1.373, C ⁴ C ⁴ 1.464, C ¹ H 1.097, C ² H 1.095, C ³ H 1.098, C ⁴ H 1.095, C ² C ¹ C ² 129, C ¹ C ² C ³ 128, C ² C ³ C ⁴ 129, C ¹ C ² H 116, C ² C ³ H 114, C ³ C ⁴ H 118;	
Phenyl	C_{2v}	C ¹ C ² 1.383, C ² C ³ 1.425, C ³ C ⁴ 1.421, C ² H 1.085, C ³ H 1.089, C ⁴ H 1.090; C ² C ¹ C ² 131, C ¹ C ² C ³ 114, C ² C ³ C ⁴ 120, C ³ C ⁴ C ³ 121;	
Benzyl	C_{2v}	C ¹ C ² 1.444, C ² C ³ 1.409, C ³ C ⁴ 1.418, C ¹ C ⁷ 1.412, C ² H 1.090, C ³ H 1.090, C ⁴ H 1.088, C ⁷ H 1.085, C ² C ¹ C ² 117, C ¹ C ² C ³ 121, C ³ C ⁴ C ³ 120, HC ⁷ H 115;	
Phenoxy	C_{2v}	C ¹ O 1.240, C ¹ C ² 1.485, C ² C ³ 1.398, C ³ C ⁴ 1.424, C ² H 1.089, C ³ H 1.091, C ⁴ H 1.089; C ² C ¹ C ² 116, C ¹ C ² C ³ 121, C ² C ³ C ⁴ 121, C ³ C ⁴ C ³ 120;	

Table II (continued)

1-Norbornyl	C _S	C ¹ C ² 1.517, C ² C ³ 1.570, C ³ C ⁴ 1.570, C ¹ C ⁷ 1.527, C ⁴ C ⁷ 1.527, C ² H 1.107, C ³ H 1.108, C ⁴ H 1.101, C ⁷ H 1.105; C ¹ C ² C ³ 98, C ² C ³ C ⁴ 103, C ¹ C ⁷ C ⁴ 88, HC ² H 106, HC ³ H 106, HC ⁷ H 106; C ⁶ C ¹ C ⁴ C ³ 117;	
7-Norbornyl	C _{2v}	C ¹ C ² 1.565, C ² C ³ 1.559, C ¹ C ⁷ 1.513, C ¹ H 1.101, C ² H(exo) 1.108, C ² H(endo) 1.109; C ⁷ H 1.072; C ¹ C ² C ³ 103, C ¹ C ⁷ C ⁴ 98, HC ² H 106; C ⁶ C ¹ C ⁴ C ³ 115, C ¹ C ⁷ HC ⁴ 180;	
ω-Butenyl	C ₁	C ¹ C ² 1.485, C ² C ³ 1.504, C ³ C ⁴ 1.341, C ¹ H 1.082, C ² H 1.118, C ³ H 1.096, C ⁴ H 1.085; C ¹ C ² C ³ 115, C ² C ³ C ⁴ 127, HC ¹ H 117, HC ² H 105, HC ⁴ H 113; C ¹ C ² C ³ C ⁴ 119;	
ω-Pentenyl	C ₁	C ¹ C ² 1.484, C ² C ³ 2.542, C ³ C ⁴ 1.505, C ⁴ C ⁵ 1.340, C ¹ H 1.082, C ² H 1.117, C ³ H 1.115, C ⁴ H 1.096, C ⁵ H 1.089; C ¹ C ² C ³ 115, C ² C ³ C ⁴ 114, C ³ C ⁴ C ⁵ 126, HC ¹ H 117, HC ² H 106, HC ³ H 106, HC ⁵ H 114; C ¹ C ² C ³ C ⁴ 180, C ² C ³ C ⁴ C ⁵ 119;	
OH	C _{∞v}	OH 0.937 (0.971) ;	a)
H ₂ O ⁺	C _{2v}	OH 0.969; HOH 113;	
O ₂ H	C _S	OH 0.976 (0.958) , OO 1.208 (1.300) ; OOH 112 (105) ;	e)
CHO	C _S	CH 1.074 (1.110) , CO 1.185 (1.171) , HCO 143 (127) ;	f)
CHO ₂	C _S	CH 1.111, CO ¹ 1.227, CO ² 1.334; HCO ¹ 126, HCO ² 114, O ¹ CO ² 120;	
CH ₂ O	C _S	CH ¹ 1.119, CH ² 1.122, CO 1.354; H ¹ CO 113, H ² CH 108, H ¹ CH ² 107;	
CH ₃ CO	C _S	CC 1.464, CO 1.186, CH 1.110; OCC 148, HCH 108;	
CH ₃ CO ₂	C _S	CC 1.529, CO ¹ 1.231, CO ² 1.339, CH 1.108; CCO ¹ 126, CCO ² 116, O ¹ CO ² 118, HCH 109;	
NH ₂	C _{2v}	NH 1.001 (1.024); HNH 104 (103);	g)
NH ₃ ⁺	D _{3h}	NH 1.009 (1.070); HNH 120 (120);	h)
CN	C _{∞v}	CN 1.154 (1.172);	a)
NO	C _{∞v}	NO 1.122 (1.151);	a)
NO ₂	C _{2v}	NO 1.174 (1.197); ONO 133 (134);	g)
	C _S	NC ¹ 1.436, C ¹ O 1.225, C ¹ C ² 1.535, C ² C ² 1.542, C ² H 1.110; C ¹ NC ¹ 107, NC ¹ C ² 112, C ¹ C ² C ² 104, NC ¹ O 120, HC ² H 107;	
CF	C _{∞v}	CF 1.263 (1.267) ;	g)
CH ₂ F	C _{2v}	CH 1.086, CF 1.305, HCH 123, HCF 119;	
CHF ₂	C _S	CH 1.089, CF 1.311; FCF 113, HCF 122;	
CF ₃	C _{3v}	CF 1.312 (1.33); FCF 115 (112);	g)
C ₂ F	C _S	CC 1.290, CF 1.268; CCF 165;	
C ₂ F ₂ ⁺	D _{2h}	CC 1.475, CF 1.291; CCF 123, FCF 115;	
CCl	C _{∞v}	CCl 1.722 (1.642);	g)
CH ₂ Cl	C _{2v}	CH 1.077, CCl 1.724; HCH 124, HCCl 118;	
CHCl ₂	C _{2v}	CH 1.077, CCl 1.715; ClCCl 120, HCCl 120;	
CCl ₃	D _{3h}	CCl 1.711 (1.740); ClCCl 120 (120) ;	g)
C ₂ Cl ₂ ⁺	D _{2h}	CC 1.437, CCl 1.742; CCCl 122, ClCCl 117;	
N ₂	C _{∞v}	N ¹ N ² 1.184, N ² N ³ 1.173, N ¹ N ³ 2.357 (2.365); N ¹ N ² N ³ 180 (180)	i)
NCO	C _{∞v}	NC 1.230 (1.230), CO 1.205 (1.18); NCO 180 (180)	j)

^a G. Herzberg, *Spectra of Diatomic Molecules*, Van Nostrand, Princeton, NJ, 1950.

^b G. Herzberg, *Spectra of Polyatomic Molecules*, Van Nostrand, Princeton, NJ, 1967.

^c Angle between the CCC plane and C¹H bond.

^d Dihedral angle between the planes C²C²C³C³ and C²C¹C².

^e M. E. Jacox and D. E. Milligan, *J. Mol. Spectrosc.*, **42**, 495 (1972).

^f J. A. Austin, D. H. Levy, C. A. Gottlieb, and H. E. Radford, *J. Chem. Phys.*, **60**, 207 (1974).

^g D. R. Stull and H. Prophet, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, No. 37 (1971).

^h W. R. Harshbarger, *J. Chem. Phys.*, **56**, 177 (1972).

ⁱ Reference 15.

^j M. W. Chase, J. L. Curnutt, A. T. Hu, H. Prophet, A. N. Syverud, and L. C. Walker, *J. Phys. Chem. Ref. Data*, **3**, 311 (1974).

have a sound basis. It is therefore most promising that the MNDO corrections take care of the observed failure of the MINDO scheme in this respect. The ethynyl radical is calculated to be linear as found by experiment.¹⁴ An interesting result is found for the fluoroethynyl radical, which MNDO-UHF predicts to deviate remarkably from linearity. The isoelectronic radicals CNO, NCO, and N₃, on the other hand, are known^{15,16} to be linear and correctly predicted to be so. Experimental data on C₂F are not available, although the Walsh rules¹⁷ suggest a linear structure. The prediction that N₃ possesses $C_{\infty v}$ symmetry rather than $D_{\infty h}$ parallels results of *ab initio* calculations.¹⁸ All cyclic alkyl radicals are found to be π -radicals with the exception of cyclopropyl, where the α hydrogen atom is tilted out-of-plane significantly. This again is on line with experiment, because reactivity data identify cyclopropyl to be a σ -type radical.¹⁹

The succinimidoyl radical structure (C₄H₄NO₂) deviates only slightly from the expected C_{2v} symmetry. Various theoretical studies^{20,21} suggest two close-lying electronic states, $^2\Pi$ and $^2\Sigma_N$. In the former, the odd electron occupies an O—C—N—C—O π -orbital and thus is spread over almost the entire molecule while in the latter ($^2\Sigma_N$), the odd electron is occupying the "lone-pair" orbital mainly localized at the nitrogen atom. MNDO-UHF predicts $^2\Pi$ to be the ground state of the radical resulting in the structure and energy given in Tables I and II. The $^2\Sigma_N$ state is predicted to be less stable by 61 kJ/mol in accordance with MNDO-HE^{20*} and *ab initio*²¹ calculations. The structure found for the $^2\Sigma_N$ radical was obtained using an appropriate starting geometry for the geometry optimization procedure and was found to be essentially identical with the STO-3G equilibrium structure.²¹

Finally, we shall focus on the structural data of the cyclic conjugated π -radicals cyclopropenyl (C₃H₃), cyclopentadienyl (C₅H₅), and tropyli radical (C₇H₇).

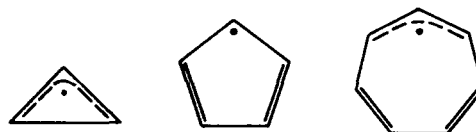
Annulene radicals have attracted the interest of many chemists,^{22–25} because they represent a class of compound for which the Jahn–Teller distortion²⁶ is to be expected, and which is small enough to allow thorough theoretical studies on almost any level of sophistication.

All these calculations predict one equilibrium structure for each radical which pseudorotates via

the alternative transition state.* Inclusion of CI is simply reducing the calculated barrier of inter-conversion^{22,24} without affecting the mentioned principle statement.

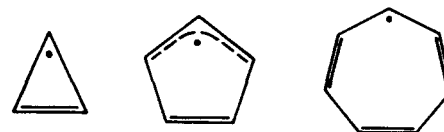
The results of our simple one-configurational calculations can be summarized as follows: The MNDO-UHF results corroborate the earlier findings²⁵ that the symmetry behavior of the electronic ground-state configuration alternates: C₃H₃ and C₇H₇ both possess 2A_2 ground states, while C₅H₅ has a 2B_1 ground-state wavefunction.

This corresponds to the following Kekulé formulas:



and the predicted bond lengths alternate accordingly. Again, there is no principal energetic preference (or "aromaticity") found either for $4n + 1$ or for $4n + 3$ electron systems.

Forcing these radicals into the corresponding alternative structures,



leads to the saddle points of one common energy hypersurface. The calculated barriers of inter-conversion (i.e., the dynamic Jahn–Teller effect) diminishes with increasing ring size in accordance with experiment.²⁵

Spin Densities

Table III summarizes the obtained correlation properties of calculated spin densities versus experimental ESR coupling constants. We used the standard procedure described by Pople and Beveridge²⁷ assuming a linear relationship between the calculated Fermi contact term (i.e., the spin population of the valence shell s -orbital, ρ_s) and the observed ESR coupling constant a :

$$a = \rho_s A \quad (11)$$

The constant A was calculated for each type of atom and the resulting correlation coefficients are given in Table III using the single-determinant and the spin-annihilated values, respectively. Unfortunately, the table reveals that MNDO-UHF spin densities compare poorly with experimental hyperfine coupling constants. We therefore do not

* MNDO-HE stands for the half-electron version of the MNDO procedure.

* See ref. 26 for a detailed description.

Table III. Correlations of calculated spin densities with experimental coupling constants. Details are given in the text, *A* values in mtesla.

Nucleus	Number of corr. points	calc. factor <i>A</i>	correlation coefficient
a) Single determinant values:			
H	88	50.45	0.627
C	23	108.4	0.923
N	5	49.74	0.940
F	3	2548.	0.933
Cl	3	562.5	0.912
b) Values after Quartet-annihilation:			
H	88	120.6	0.399
C	23	110.3	0.773
N	5	51.8	0.967
F	3	4948.	0.962
Cl	3	1686.	0.911

tabulate the individual results in detail; such a table is available upon request.

The origin of this poor correspondence between theory and experiment can be due to various reasons. We suppose that the inclusion of limited configuration interaction might improve the predicted ESR coupling constants. Such an approach would, however, call for a complete reparametrization of the procedure.

CONCLUSIONS

The represented results clearly show that MNDO-UHF calculations can be used successfully to estimate thermodynamical and structural data of doublet systems. The limits of confidence are not substantially worse than for closed-shell species. The good agreement achieved for a variety of very different ground-state properties briefly discussed in this work corroborate independently the choice of parameters met by Dewar and Thiel.²

Nevertheless, the calculation of ESR coupling constants in its present state does not seem feasible for assigning experimental data.

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* Note, that for the cyclobutadiene radical cation and other even-numbered annulene radicals, the two stationary points (equilibrium structure and saddle-point) are found along two *different* modes of vibration. This leads to a rectangular (equilibrium structure) and a rhomboidal (saddle-point) geometry, respectively.