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A MNDO study of carbon clusters with specifically fitted parameters

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Summary. A MNDO method with new parameters for carbon clusters is presented. The parameters in the new sets are specifically tuned to fit the properties of small carbon clusters, C_2, C_3,C_5 and C_7–C_{10}, and buckminsterfullerene, C_{60}. The validity of these MNDO parameters is verified by experimental data. The calculated (with new parameters) IR spectra of C_{60} and the heat of formation, geometry and IR spectra of C_{70} agree satisfactorily with observed data. Heats of formation of other fullerenes, from C_{20} to C_{84}, and $C_{60}O$ are evaluated. The resulting heats of formation of the isomers of C_{76} and C_{84} are reliable and their relative stability is in excellent agreement with other reports. The predicted IR spectra of several fullerenes, $C_{24}(C_{6v})$, $C_{28}(T_d)$, $C_{32}(D_3)$, $C_{36}(D_{6h})$, $C_{50}(C_{5h})$ and $C_{80}(D_{5d})$ are provided to aid assignments of experimental spectra.

Key words: Carbon cluster – Fullerene – Semiempirical methods – MNDO

Introduction

Since the discovery of C_{60} [1], fullerenes, the special carbon-caged compounds, have built their own chemistry. Numerous experiments [2–13] and theoretical studies [2, 14–23] were made to investigate compounds in this family and their derivatives. High level *ab initio* computations provide the best theoretical model for fullerenes just as for any other compounds, but for compounds of the size of fullerenes they are generally expensive and may be limited by computational resources. Several other treatments including MNDO [24], AM1 [25], PM3 [26], Hückel, tight-binding, and MM [27] computations, are applied to fullerenes [18, 19, 28–35]. These methods generally predict reasonable geometries and correctly identify the most stable isomers, but relative energies may occasionally be less accurate.

In a new and exciting field such as fullerenes, an accurate and rapid theoretical modeling tool is desirable to estimate both their properties and those of their

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derivatives. The improvement of an existing scheme is expedient for this purpose. Semiempirical methods are extensively applied to study fullerenes and their derivatives, and much data has been accumulated. For example, the MNDO method was used to test diverse fullerenes and their IR spectra. According to the literature, MNDO evaluated the relative energies [18] of the most stable isomers of C_{84} satisfactorily [32, 35–38], but heats of formation of C_{60} and C_{70} exceeded experimental values by about 100 kcal/mol [4–7, 39]. The heats of formation of other fullerenes show similar differences by comparison with calculations calibrated for this property [18, 19]. This deficiency of MNDO likely reflects the fact that these parameters were obtained by fitting the properties of carbon in organic compounds [24] that differ from fullerenes. Martin et al. [40] reported that a reoptimization of MNDO parameters improved the properties of small carbon clusters, C_2 to C_{10}. However, we [41] verified that the properties of some tested fullerenes (C_{20}, C_{24} and C_{60}) were not improved satisfactorily when the set of MNDO parameters by Martin et al. was applied as pointed out in Ref. [40]. C_{60} molecule is well investigated and many experimental results are reported including the geometry [11] and heats of formation for both polycrystalline and gaseous phases [4–7]. In the present work, we included the data on C_{60} with accurate data on small clusters to reoptimize the MNDO parameters. This scheme of MNDO with the new parameters is then applied to other fullerenes to test its validity. Geometries according to the new scheme were improved to a level comparable to the results of *ab initio* calculations. Heats of formation were as good as those from SCF/STO-3G followed by calibration to an idealized graphitic sheet with an equal number of carbon atoms [19, 39]. Heats of formation of fullerene isomers are also examined. The calculated IR spectra of C_{60} and C_{70} agreed satisfactorily with observed data.

Optimization of parameters and computational details

The seven MNDO parameters U_{ss}, U_{pp}, β_s, β_p, ζ_s, ζ_p and α [24], were optimized specifically for carbon in carbon clusters. The parameters in the new sets were deduced by minimizing the errors between calculated and reference data, which were obtained either from experiment [42] or from high-level *ab initio* calculations [43]. The optimization was carried out by minimizing the sum of squares of residuals between calculated and referenced values multiplied by a corresponding weighting factor, which was introduced in MNDO [24] such that the sum to be minimized was dimensionless and properly weighted. These weighting factors are defined as 1 mol/kcal for heats of formation, 10 eV^{-1} for ionization potentials, 100 $\mathrm{Å}^{-1}$ for bond lengths and 1 deg^{-1} for bond angles [24]. The optimization was implemented with a quasi-Newton method with the second derivative Hessian updated with the BFGS algorithm [44] and by nonlinear least-square fitting; both methods yielded the same finally optimized parameters.

The reference data for optimization included heats of formation, geometry, and ionization potentials of small carbon clusters (C_2, C_3, C_5 and C_7–C_{10}) [42, 43], and the heat of formation and geometry of C_{60} [4, 11]. Eight parameters of C_{60} were utilized to optimize the MNDO parameters. Two geometric properties, the six–six ring bond length (r_{6-6}) and six–five ring bond length (r_{6-5}), with the heat of formation of C_{60} were used as reference data. To maintain the icosahedral symmetry of C_{60}, bond angles of two types and dihedral angles of three types were constrained during optimization. The other reference data were taken from small

Table 1. MNDO parameters for carbon atoms in carbon clusters

Parameters	Standard set[a]	Set A[b]	Set B[c]
U_{ss}	− 52.279745	− 52.244770	− 52.253460
U_{pp}	− 39.205558	− 39.237106	− 39.215668
β_s	− 18.985044	− 19.007509	− 18.977848
β_p	− 7.934122	− 7.845510	− 7.849880
ζ_s	1.787537	1.811052	1.806560
ζ_p	1.787537	1.781326	1.780856
α	2.546380	2.565411	2.566805

[a] Ref. [24].
[b] Fitted with $\Delta H_f(C_{60}) = 635.05$ kcal/mol.
[c] Fitted with $\Delta H_f(C_{60}) = 599.43$ kcal/mol.

carbon clusters. The reference properties of C_2, C_3, and C_5 were experimental values [42]. The reference data of C_7–C_{10} were assembled from coupled cluster CCD + ST(CCD)/6–31G* calculations [43] including three bond lengths of C_7, four bond lengths of C_9, and one bond length plus two bond angles of C_{10}. Two measured values of heat of formation of C_{60} are used to reparametrize MNDO parameters separately resulting in new parameters in two sets: set A corresponding to $\Delta H_f(C_{60})$ being 635.05 kcal/mol [4] and set B corresponding to $\Delta H_f(C_{60})$ being 599.43 kcal/mol [7]. The effect of varied values of heat of formation of C_{60} on the computed properties of fullerenes is discussed in the next section. These MNDO parameters in two sets are listed in Table 1 with standard carbon MNDO parameters.

The first step in our fullerene computation was MM3 [27] geometry optimization with the SPARTAN 3.0 package [45]. Semiempirical calculations or *ab initio* calculations then followed with MOPAC 93 [46] or GAUSSIAN-92 [47]. During optimization, when the gradients were evaluated with finite differences, updating of parameters was effected on varying the parameters of the carbon atom in the BLOCK area of MOPAC 93 code. This variation can also be implemented with the keyword EXTERNAL.

Results and discussion

The reference data computed according to the MNDO method with the new parameters are summarized in Tables 2 and 3 with calculated values according to other semiempirical methods (AM1, PM3 and MNDO with standard parameters), and *ab initio* results of C_{60} [14, 15]. The MNDO results with the new parameters increase the accuracy of computed properties for all reference molecules and particularly show significantly improved properties of C_{60}. Generally, the standard semiempirical methods overestimate heats of formation of carbon clusters. For small carbon clusters, AM1, PM3 and MNDO (with standard parameters) overestimate heats of formation by average errors 41.5, 35.7 and 40.4 kcal/mol, respectively. Clearly MNDO with the new parameters has smaller errors 21.00 and 19.36 kcal/mol for sets A and B, respectively. There are four reports [4–7] on the experimental heat of formation of crystalline C_{60}. The heat of formation in gaseous phase is estimated to be either 635 or 600 ± 1 kcal/mol from the observed heat of

Table 2. Semiempirical results and reference properties of small carbon clusters

Compounds		AM1	PM3	MNDO/ standard	MNDO/A^b	MNDO/B^c	Reference data^c
C_2	ΔH_f^d	216.25	258.23	235.43	227.08	227.34	200.22
	IP^e	12.27	11.71	11.66	11.75	11.73	12.1
	r^f	1.164	1.189	1.169	1.160	1.161	1.243
C_3	ΔH_f	212.45	206.65	220.33	213.26	212.64	196.00
	IP	11.33	11.75	11.04	11.01	11.00	11.4
	r	1.288	1.189	1.290	1.283	1.284	1.287
C_5	ΔH_f	270.13	266.42	275.33	261.18	260.02	234.00
	IP	10.94	10.95	10.37	10.45	10.43	10.7
	r_1	1.280	1.279	1.285	1.278	1.278	1.275
	r_2	1.278	1.278	1.281	1.274	1.275	1.271
C_7	ΔH_f	330.85	327.64	331.16	310.13	308.43	298.50
	IP	10.09	10.11	9.58	9.64	9.62	10.0
	r_1	1.279	1.277	1.283	1.276	1.277	1.280
	r_2	1.279	1.281	1.283	1.276	1.276	1.270
	r_3	1.267	1.270	1.273	1.266	1.266	1.264
C_8	ΔH_f	417.89	378.48	400.92	376.27	373.28	338.30
	IP	9.23	9.17	8.97	8.99	8.98	9.2
	r_1	1.381	1.394	1.391	1.391	1.383	1.380
	r_2	1.225	1.221	1.227	1.227	1.221	1.240
C_9	ΔH_f	391.35	388.69	386.61	358.71	356.46	353.00
	IP	9.56	9.58	9.07	9.14	9.12	9.4
	r_1	1.277	1.276	1.282	1.275	1.276	1.269
	r_2	1.281	1.283	1.284	1.277	1.278	1.283
	r_3	1.265	1.267	1.271	1.264	1.265	1.261
	r_4	1.268	1.221	1.274	1.267	1.268	1.269
C_{10}	ΔH_f	403.90	376.35	385.43	353.01	350.00	332.60
	IP	9.81	9.77	9.46	9.51	9.50	—^{g}
	r	1.234	1.228	1.230	1.224	1.224	1.290
	θ_1^h	143.96	143.98	143.19	143.99	143.99	119.40
	θ_2	144.01	144.04	144.02	144.00	144.00	168.60
Average error							
	ΔH_f	41.46	35.69	40.37	21.00	19.36	

[a] C_2–C_5 are experimental values from Ref. [42] and C_7–C_{10} are *ab initio* values from Ref. [43].
[b] Fitted with $\Delta H_f(C_{60}) = 635.05$ kcal/mol.
[c] Fitted with $\Delta H_f(C_{60}) = 599.43$ kcal/mol.
[d] In kcal/mol.
[e] In eV.
[f] In Å.
[g] Not available.
[h] In degree.

formation in the crystalline phase with correction for heat of sublimation from experimental measurement [4, 7, 39, 48]. The choice of heat of formation of C_{60} as a reference data in reparametrization affects mainly heats of formation of carbon clusters. Set *B*, optimized with $\Delta H_f(C_{60})$ being 599.43 kcal/mol, provides superior estimates of heats of formation. According to the geometric data in Tables 2 and 3,

Table 3. Heat of formation (kcal/mol) and bond lengths (Å) of C_{60}

C_{60}	SCF/[a] STO-3G	MP2/[b] TZP	AM1	PM3	MNDO/ standard	MNDO/ set *A*	MNDO/ set *B*	Experi- ment
ΔH_f	625.00	—	972.39	810.81	868.22	635.04		635.05[c]
							599.43	599.43[d]
r_{6-5}	1.463	1.446	1.464	1.458	1.474	1.465	1.465	1.458[e]
r_{6-6}	1.376	1.406	1.385	1.384	1.400	1.392	1.392	1.401[e]
Error	0.015	0.009	0.011	0.009	0.009	0.008	0.008	—

[a] Ref. [14].
[b] Ref. [15].
[c] Ref. [4].
[d] Ref. [7].
[e] Ref. [11].

the new MNDO parameters yield the geometry of the reference molecules to the accuracy of *ab initio* computations [14, 15, 43]. The geometries obtainedwith MNDO parameters in sets *A* and *B* are essentially the same, but those in set *A* yields slightly superior ionization potentials for all reference small carbon clusters.

The new MNDO parameters were justified to be improved by tests on fullerenes of which the properties were not included as reference data. Properties of several fullerenes were computed to test the behavior of the new parameters. First, the heat of formation and geometry of C_{70}, for which experimental data [6, 49] exist for comparison, were investigated. Second, heats of formation of fullerenes containing 20–84 carbon atoms and some derivatives of C_{60} were evaluated for comparison with those computed with other methods [39], and the relative stability of isomers of C_{76} and C_{84} was examined. Third, the IR frequencies [8–10] of C_{60} and C_{70}, not included in the optimization, were examined.

The geometry of C_{70} [49, 50] serves as an ideal test of the new parameters of MNDO. The structure of this molecule of symmetry D_{5h} is characterized by bond lengths of eight types shown in Fig. 1. The results of MNDO computations with standard and new parameters are listed in Table 4 with *ab initio* [50] and experimental results [49] from literature. The values calculated with MNDO and new parameters in both sets deviate by 0.008 Å on the average, comparable to the SCF deviations 0.007–0.009 Å whereas MNDO with standard parameters yields an average deviation 0.016 Å. The improvement is significant in the sense that bond lengths of all eight types are corrected to the same precision. The heat of formation of C_{70} is measured to be 2621 kJ/mol (627 kcal/mol) [6, 39]. The same group reported the heat of formation of C_{60} to 599 kcal/mol, similar to the value used to fit our parameter set *B*. The heat of formation of C_{70} evaluated with MNDO and modified parameter set *B* is 624.3 kcal/mol, within 3 kcal/mol of the experimental values. Application of the modified MNDO parameters to C_{70} indicated that the new parameters satisfactorily adjusted to apply to fullerenes. Table 1 shows that the adjustment of parameters in our scheme is very small, but these small variations suffice to improve the description of fullerenes.

The heats of formation of some fullerenes, ranging from C_{20} to C_{84} and $C_{60}O$ according to various methods are summarized in Table 5. Standard semiempirical methods MNDO, AM1 and PM3 show considerably larger heats of formation.

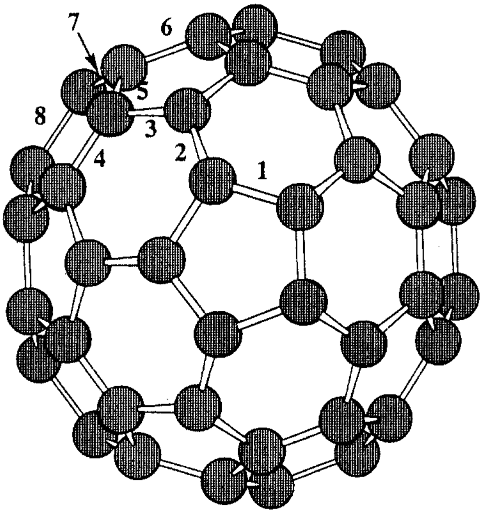

Fig. 1. C_{70} molecule with bonds of various types labeled to specify the geometry

Table 4. Bond lengths (Å) of C_{70}

C_{70} Bond Index	SCF/[a] STO-3G	SCF/[a] DZ	SCF/[a] DZP	MNDO/ standard	MNDO/ set *A*	MNDO/ set *B*	Experiment[b]
1	1.417	1.413	1.415	1.442	1.434	1.434	1.430
2	1.379	1.370	1.375	1.402	1.393	1.393	1.380
3	1.364	1.357	1.361	1.389	1.380	1.381	1.370
4	1.414	1.402	1.407	1.430	1.422	1.422	1.407
5	1.470	1.455	1.457	1.478	1.470	1.469	1.460
6	1.461	1.450	1.451	1.473	1.467	1.463	1.458
7	1.486	1.474	1.475	1.484	1.477	1.478	1.476
8	1.455	1.445	1.446	1.469	1.460	1.460	1.459
Error	0.008	0.009	0.007	0.016	0.008	0.008	

[a] Ref. [50].
[b] Ref. [49].

The heat of formation with MNDO and the new parameters shows the promising character that it generally agrees with *ab initio* values deduced from SCF/STO-3G computations [19] followed by corrections to an idealized graphitic sheet with carbon atoms in an equal number.

The most stable isomer of a particular size fullerene is an interesting problem. The heats of formation of two isomers of C_{76} [29, 33] and six most stable isomers of C_{84} [32, 35, 51] are listed in Table 5. The more stable isomers of higher fullerenes follow the isolated pentagon rule [52, 53]; thus, only isomers that obey this rule are considered. The number of such isomers are respectively, two and twenty-four for C_{76} and C_{84} [51]. All twenty-four C_{84} isomers are computed [54] with the MNDO method with new parameters and the more stable ones are identified. For C_{76}, the D_2 isomer is more stable by 18 kcal/mol than the T_d isomer. The D_2 isomer is the only isomer of C_{76} observed experimentally [37]; thus the large energy difference

Table 5. Heats of formation (kcal/mol) of fullerenes from semiempirical calculations

	AMI	PM3	MNDO/ standard	MNDO/ set *A*	MNDO/ set *B*
$C_{20}(D_{5d})$	881.7	770.3	834.8	749.5	737.3
$C_{24}(C_{6v})$	905.9	776.4	850.2	758.5	744.0
$C_{28}(T_d)$	958.3	851.2	937.2	775.9	746.9
$C_{32}(D_3)$	940.9	803.0	875.4	751.6	732.4
$C_{36}(D_{6h})$	1052.6	840.8	925.1	772.1	744.9
$C_{50}(C_{5h})$	1022.0	864.5	922.2	704.2	673.8
$C_{60}(I_h)$	972.4	810.8	868.2	634.9	599.4
$C_{70}(D_{5h})$	1062.0	884.2	939.3	665.7	624.1
$C_{76}(D_2)$	1122.3	934.2	988.7	691.4	646.5
$C_{76}(T_d)$	1147.0	959.5	1006.5	709.4	664.5
$C_{78}(C'_{2v})$	1133.2	942.7	992.1	688.6	643.1
$C_{80}(D_{5d})$	1216.0	1022.1	1060.3	749.6	701.0
$C_{84}(D_{2d})$ **23**[a]	1165.2	966.4	1013.5	684.6	634.9
$C_{84}(D_2)$ **22**	1165.2	966.9	1013.9	685.0	635.4
$C_{84}(D_{6h})$ **24**	1173.3	973.3	1021.4	692.5	642.9
$C_{84}(C_s)$ **16**	1173.1	973.3	1021.6	692.6	643.1
$C_{84}(D_{3d})$ **19**	1173.2	973.7	1021.8	693.0	643.4
$C_{84}(C_2)$ **11**	1173.1	973.3	1022.2	693.5	643.8
$C_{60}O(C_{2v})$	960.2	791.8	839.8	600.8	564.4
$C_{60}O(C_s)$	947.8	785.3	834.0	597.2	561.3

[a] Isomers of C_{84} are numbered according to Ref. [51].

confirms the experimental results. According to other theoretical calculations the stabilization of the D_2 isomer relative to the T_d isomer is 14.9 kcal/mol [55] or 42.7 kcal/mol at the SCF/DZ level of theory [33]; further *ab initio* calculations with larger basis sets are required to resolve this discrepancy. The orders of the six most stable isomers of C_{84} produced from MNDO with new parameters in the two sets and with standard parameters [35] are identical. For parameter set *B*, D_{2d} **23** is predicted to be most stable, with the D_2 **22** slightly higher by 0.5 kcal/mol. The next group consists D_{6h} **24**, C_s **16**, C_{3d} **19** and C_2 **11** with energies relative to D_{2d} **23** in the range 8.0–8.9 kcal/mol. A tight-binding calculation [32] provided the same six structures as the most stable isomers with alternations as follows: D_2 **22** most stable and D_{2d} **23** second in the list, and C_2 **11** and C_{6h} **24** are switched. The result of calculation at the HF/*sv7s4p* level [35] is same as with MNDO that D_{2d} **23** is slightly lower in energy by 0.4 kcal/mol than D_2 **22**. LDF [32] yields results similar to those of the tight-binding computation regarding the relative energy of the two most stable isomers. NMR spectra of C_{84} [37, 38] indicate a mixture of D_2 **22** and D_{2d} **23** in the ratio 2:1. The structure of a single crystal of the metal adduct $(\eta^2\text{-}C_{84})$ $Ir(CO)\,Cl(PPh_3)_2{\cdot}4C_6H_6$ shows that the carbon cage has a D_{2d} **23** structure [56]. This observation confirms that D_{2d} **23** is one of the most stable isomers. All evidence indicates that D_2 **22** and D_{2d} **23** are the most stable isomers of C_{84} and are nearly isoenergetic.

MNDO parameters in the new sets were also applied to fullerene derivatives. $C_{60}O$ [57–59] has two stable isomers; one is epoxide-like with C_{2v} symmetry and the other is bridged anulene-like with C_s symmetry. The relative stability of the two isomers predicted according to computations at various levels disagree with the

Table 6. IR frequencies (cm^{-1}) of C_{60}

Mode	Experiment[a] solid state	Experiment[b] Gaseous phase	Hückel[c]	MNDO/set *A* scaled by 0.85	MNDO/set *B* scaled by 0.85
$1f_{1u}$	528	527.1	472	493.6	493.6
$2f_{1u}$	577	570.3	618	614.0	614.5
$3f_{1u}$	1183	1169.1	1119	1156.1	1157.1
$4f_{1u}$	1429	1406.9	1434	1393.3	1394.8
Error	—	—	5.8%	4.0%	4.0%

[a] Ref. [8].
[b] Ref. [9].
[c] Ref. [60].

Table 7. IR spectra of C_{70}, frequencies (cm^{-1})

Mode	MNDO/standard scaled by 0.85		MNDO/set *A* scaled by 0.85		MNDO/set *B* scaled by 0.85		Experiment[a]	
a''_2	418	*w*	421.0	*m*	420.9	*m*	458.2	*m*
e'_1	533	*w*	535.7	*m*	535.6	*m*	535.5	*ms*
e'_1	553	*w*	555.5	*m*	555.4	*m*	565.7	*m*
a''_2	630	*w*	600.2	*mw*	600.2	*mw*	578.0	*s*
e'_1	701	*w*	631.9	*m*	631.7	*m*	642.2	*ms*
a''_2	790	*m*	659.0	*w*	658.6	*w*	674.2	*ms*
e'_1	893	*w*	790.3	*m*	790.5	*m*	795.1	*s*
e'_1	1061	*w*	1067.9	*mw*	1068.2	*mw*	1087.0	*w*
e'_1	1117	*m*	1124.4	*w*	1125.2	*w*	1133.2	*mw*
a''_2	1322	*m*	1135.4	*w*	1135.7	*w*	1141.0	*s*
e'_1	1353	*vs*	1419.5	*s*	1420.6	*s*	1430.7	*vs*
e'_1	1391	*m*	1471.3	*ms*	1472.5	*ms*	1461.0	*m*
Error	7.4%		1.9%		1.9%			

[a] Ref. [10].

available experimental evidence. Heats of formation of $C_{60}O$ in two isomers are listed in Table 5. Semiempirical computations indicate that the C_s isomer is more stable than the C_{2v} isomer by 12.4, 6.5, 5.8, 3.6 and 3.1 kcal/mol for AM1, PM3, MNDO (standard parameters), MNDO (modified parameter set *A*) and MNDO (modified parameter set *B*), respectively. First principle calculations indicate that C_s is more stable than C_{2v} by 9.3, 2.2 and 1.1 kcal/mol for HF/3–21G, HF/6–31G* and LSD/DZP computations. The value becomes − 0.5 kcal/mol for an NLSD/DZP calculation [59]. The MNDO method with new parameters predicts energies similar to *ab initio* calculations.

IR spectra of C_{60} and C_{70} are reported and can serve to test the validity of the new MNDO parameters. The characteristic IR frequencies of C_{60} by MNDO with the new parameters and those from experimental measurements [10] in solid state and in gaseous phase are listed in Table 6. Table 6 presents also the values estimated by Cyvin et al. [60] from a normal-coordinate analysis with a five-parameter force field based on a Hückel molecular orbital analysis. This lengthy procedure resulted in an average deviation 45.0 cm^{-1}. The current results of

Table 8. Simulated IR frequencies (cm^{-1}) (scaled by 0.85) and relative intensities of fullerenes by MNDO/set B for carbon

Fullerenes	Frequency (Symmetry class, Relative intensity)				
$C_{24}(C_{6v})$	$666.9(a_1,s)$	$832.7(a_1,m)$	$900.4(e_1,m)$	$1102.9(a_1,s)$	$1220.7(e_1,m)$
$C_{28}(T_d)$	$502.7(a_1,w)$	$615.7(a_1,w)$	$622.7(a_1,w)$	$626.6(a_1,w)$	$655.6(a_1,w)$
	$661.9(a_1,m)$	$668.5(a_1,s)$	$670.4(a_1,w)$	$680.8(a_1,s)$	$693.7(a_1,s)$
	$722.9(a_1,vs)$	$737.3(a_1,m)$	$737.6(a_1,w)$	$740.3(a_1,w)$	$743.2(a_1,s)$
	$803.7(a_1,s)$	$837.5(a_1,s)$	$966.7(a_1,m)$	$980.9(a_1,m)$	$983.7(a_1,s)$
	$983.3(a_1,s)$	$1002.6(a_1,s)$	$1040.2(a_1,w)$	$1083.2(a_1,w)$	$1092.6(a_1,s)$
	$1134.2(a_1,m)$	$1145.5(a_1,m)$	$1160.5(a_1,s)$	$1167.8(a_1,s)$	$1180.7(a_1,s)$
	$1201.8(a_1,s)$	$1202.6(a_1,w)$	$1238.3(a_1,m)$	$1240.9(a_1,m)$	$1243.9(a_1,w)$
	$1331.7(a_1,s)$	$1335.4(a_1,w)$	$1345.2(a_1,w)$	$1353.2(a_1,w)$	$1369.7(a_1,w)$
	$1402.6(a_1,m)$	$1412.9(a_1,s)$			
$C_{32}(D_3)$	$303.1(e,m)$	$422.2(e,m)$	$423.4(a_2,s)$	$485.2(e,w)$	$526.4(e,w)$
	$572.3(a_2,w)$	$601.3(e,m)$	$633.0(e,s)$	$634.8(a_2,s)$	$661.4(a_2,s)$
	$687.2(a_2,s)$	$729.1(e,s)$	$741.0(e,m)$	$758.6(a_2,s)$	$762.3(e,s)$
	$814.8(e,s)$	$834.1(a_2,s)$	$958.1(e,m)$	$974.8(e,s)$	$1053.9(a_2,m)$
	$1062.7(e,m)$	$1079.3(e,s)$	$1130.5(e,w)$	$1145.5(a_2,s)$	$1161.7(e,m)$
	$1202.9(a_2,s)$	$1226.6(e,m)$	$1234.0(e,s)$	$1305.9(e,m)$	$1436.0(e,w)$
$C_{36}(D_{6h})$	$427.3(e_{1u},w)$	$461.0(a_{2u},s)$	$674.3(e_{1u},w)$	$748.0(e_{1u},w)$	$767.4(a_{1u},s)$
	$812.8(a_{2u},s)$	$1084.8(e_{1u},w)$	$1098.3(a_{2u},s)$	$1192.3(e_{1u},w)$	$1232.2(a_{2u},s)$
	$1256.3(e_{1u},m)$	$1343.7(e_{1u},w)$			
$C_{50}(C_{5h})$	$341.5(a'',w)$	$508.9(e'_1,m)$	$649.9(a'',w)$	$687.5(e'_1,s)$	$687.5(e'_1,m)$
	$702.9(e'_1,s)$	$756.2(e'_1,s)$	$985.1(e'_1,w)$	$1051.5(a'',s)$	$1079.6(e'_1,w)$
	$1182.5(a'',w)$	$1199.1(e'_1,w)$	$1341.2(e'_1,s)$	$1360.5(e'_1,s)$	$1432.4(e'_1,s)$
	$1448.3(a'',w)$				
$C_{80}(D_{5d})$	$256.0(a''_2,m)$	$299.9(a''_2,w)$	$410.8(a''_2,m)$	$440.6(e'_1,w)$	$531.5(e'_1,m)$
	$534.5(a''_2,w)$	$537.3(e'_1,s)$	$575.9(e'_1,m)$	$619.3(e'_1,m)$	$649.9(e'_1,m)$
	$653.3(e'_1,m)$	$682.7(e'_1,w)$	$760.2(e'_1,m)$	$794.3(a''_2,s)$	$890.0(a''_2,s)$
	$1077.5(e'_1,m)$	$1101.4(a''_2,s)$	$1114.7(e'_1,s)$	$1119.7(a''_2,s)$	$1143.8(e'_1,s)$
	$1223.4(e'_1,s)$	$1240.6(a''_2,m)$	$1246.5(a''_2,s)$	$1259.7(e'_1,m)$	$1275.7(e'_1,m)$
	$1314.6(a''_2,s)$	$1329.5(e'_1,w)$	$1334.0(e'_1,s)$	$1357.9(e'_1,vs)$	$1369.2(a''_2,w)$
	$1387.9(a''_2,s)$	$1411.2(a''_2,s)$	$1426.1(e'_1,m)$	$1432.8(e'_1,w)$	$1436.9(a''_2,s)$

MNDO with new parameters shown in Table 6 scaled by 0.85 (derived by least-square fitting) deviate by 25.4 cm^{-1}. A scaling factor in the range 0.70–0.90 [10] is generally applied for semiempirical frequencies for adequate assignment of experimental data. A vibrational analysis of C_{70} was also made. The least-square fitting to experimental values yielded a uniform scaling factor 0.85. The scaled C_{70} frequencies shown in Table 7 deviate from experimental values [10] by 12.9 cm^{-1} on average, superior to estimates from MNDO with standard parameters. The intensities of bands at large wavenumbers agree well, but not at small wavenumbers. The average error of wavenumber computation with MNDO and the new parameters is 4.0% for C_{60} and 1.9% for C_{70}, both with a constant scaling factor 0.85. This accuracy is acceptable, particularly when *ab initio* computations are difficult. IR spectra, both the frequencies and relative intensities, of fullerenes, $C_{24}(C_{6v})$, $C_{28}(C_1)$, $C_{32}(D_3)$, $C_{36}(D_{6h})$, $C_{50}(C_{5h})$, and $C_{80}(D_{5d})$ were also computed with MNDO and the new parameters. The results are summarized in Table 8 for the vibrational frequency (scaled by 0.85), symmetry class and relative intensity. As the T_d symmetry of C_{28} was not retained during the computation C_{28} was reported as C_1 symmetry. The wavenumbers are expected to be reliable but the relative intensities must be viewed with caution, as indicated by the previous experiments on C_{60} and C_{70}. Generally, the relative intensities at high frequencies are likely more reliable than those for modes at low frequency. These simulated IR spectra with MNDO and the new parameters may provide guidance for assignment of IR spectra. In summary, the MNDO method with new parameters improves the properties of fullerenes over the standard parameters; bond lengths are uniformly reduced by 0.007–0.009 Å, relative energies of isomers remain constant to within 0.2 kcal/mol, and vibrational frequencies show unsymmetric variations to provide better predictions.

Conclusions

Our MNDO parameters for carbon atoms in carbon clusters was deduced from the optimization of the geometric parameters, heats of formation and ionization potentials of small carbon clusters, C_2, C_3, C_5 and C_7–C_{10}, and C_{60}. The evaluation of the reference data by the new scheme shows excellent convergence. The properties of the reference data computed with MNDO and the new parameters are generally in better agreement with the experimental or high level *ab initio* results than those computed by standard semiempirical methods. The application of this new scheme to fullerenes of which properties were not included in the reference data set for the reparametrization further demonstrated the validity of this new scheme. The evaluation of IR spectra of C_{60} is an example. The properties obtained for C_{70}, including geometry, heat of formation and IR spectra, are satisfactory. The heat of formation of C_{70} agrees with the experimental measurement [6, 39] to within 3 kcal/mol. Heats of formation of several fullerenes and a functionized fullerene, $C_{60}O$, computed with MNDO and the new parameters are closer to the calibarated *ab initio* results than those computed by standard semiempirical methods. The relative stability of C_{76} and C_{84} agrees with other reports [32, 33, 35]. This new scheme was also applied to evaluate IR spectra of several fullerenes, yielding spectra to help the assignment of experimental data. In the future, a reoptimization of the parameters taking some experimental results of larger fullerenes and functionized fullerenes, when the experimental data are available, as references data would potentially produce better results than the set of MNDO parameters presented in this report.

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