

Van Der Waals Surface Areas and Volumes of Fullerenes

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We present calculations of van der Waals (vdW) surface area (S) and volume (V) for a variety of carbon fullerene molecules ranging from C_{20} to C_{240} . Also reported are calculations of the inner vdW cavity volume and of the nuclear framework surface area and volume (S_n and V_n). The vdW radius r of a carbon atom is not uniquely defined, so our S and V values are generated for $r_{\min} = 1.47 \text{ \AA}$ and $r_{\max} = 1.76 \text{ \AA}$. Calculation of S and V at intermediate r values indicates that simple linear interpolation between the (r_{\min} , r_{\max}) limits is accurate to within 1%. We also find that S_n can be calculated to within 1% of the actual value for C_{60} and larger fullerenes by assuming all bonds have the C–C bond length of graphite (1.415 \AA).

Introduction

One question about fullerenes is “how big are they?” Two quantities measuring size are the surface area (S) and the volume (V). S and V of the nuclear framework differ from S and V of the van der Waals (vdW) framework (the nuclear framework inflated by the vdW surface which encloses the molecule). We label the nuclear framework values as S_n and V_n and the vdW values as S and V .

The calculations of S and V reported here were motivated, in part, by practical considerations related to extraction and purification of fullerenes. Differences in S and V may be related to differences in retention times on chromatography columns. In addition, since the rigid, well-defined geometries of fullerenes should make theoretical approaches to calculating solubility (such as scaled particle theory¹) feasible, knowledge of S and V should be useful in the prediction and rationalization of their solubilities. V measures the cavity volume of the solvent, and S is related to the average binding energy of the fullerene with the solvent shell, at least if one assumes that the energetics of its interaction with the solvent molecule (such as CS_2) is dominated by the vdW interaction. The solubility of C_{60} has been extensively studied,^{2,3} and the solubility of C_{70} has recently been determined in a variety of solvents;⁴ but, to date, there has been little work on the solubility of other fullerenes.

Knowledge of S and V may be useful in other ways. For example, the molecular (vdW) volume of C_{60} has recently been calculated^{5,6} to evaluate its potential utility in binding to (and thereby blocking) the active site of the HIV-protease enzyme. Other possible applications include prediction of solid densities, packing, and enthalpies of sublimation.

Knowledge of S_n and V_n is, as we discuss below, of interest because they can be used to predict the energetics, and hence stability, of fullerenes. Finally, another quantity related to the size of a fullerene is the inner cavity volume. This is of interest when considering the encapsulation of atoms or molecules within the shell, such as the encapsulation of He and Ne in C_{60} .⁷

Methods

The coordinates we have used in these calculations are the result of first-principles quantum molecular dynamical (QMD)

relaxation simulations using the local-orbitals-based method⁸ with the local orbitals confined within a radius of 3.3 bohr. The energies per atom obtained with these simulations are included in Table 1. The method has previously been used successfully to simulate C_{60} as well as larger fullerenes.^{9,10} For C_{60} , it yields bond lengths of 1.398 and 1.442 \AA and a molecular radius of 3.53 \AA .

To calculate the nuclear framework surface area of each fullerene (S_n), extra vertices are added at the centers-of-mass of each five- and six-membered ring. The surface is thus divided into triangles (Figure 1b), and S_n is the sum of the areas of the newly created triangles. Similarly, the volume of the fullerene, V_n , is the sum of the volumes of the irregular tetrahedra created by each triangle and the center-of-mass of the fullerene molecule.

To calculate a vdW volume V for each molecule a sphere of radius $r \text{ \AA}$ is centered on each atom (Figure 1c). These interpenetrating spheres form a structure with an inner and outer surface. We then determined numerically the outer surface area, S , the volume enclosed by the outer surface, V , and the volume enclosed by the inner surface, the “inner cavity volume”. For the volume integrations we used a ΔV of 0.001 \AA^3 , and for the surface integrations the largest ΔS was less than 0.001 \AA^2 .

The vdW radius r may be determined by the distance between the fullerene molecules in solid C_{60} (Figure 2). Assuming a radius of 3.53 \AA for C_{60} and a separation of 10.0 \AA , we arrive at a vdW radius for the individual carbon atoms of 1.47 \AA . This is half the shortest nonbonded C–C distance, assuming that each of the separated C_{60} molecules has an atom on the line between their centers-of-mass. However, if the separated molecules are aligned six-membered ring to six-membered ring, then half the shortest C–C distance is 1.76 \AA . In the calculations, we have used each of the two extremes as well as two intermediate values, 1.58 and 1.68 \AA , at which the merit of linear interpolation between the extreme values has been examined. For V , S , and the vdW sphere volume, the difference between a linear interpolation value and the calculated value is always less than 1.0%. A commonly used value for the vdW radius of C is 1.7 \AA . In ordered solid C_{60} the average of the shorter nonbonded C–C distances is 3.44 \AA (shortest 3.14 \AA),¹¹ and in graphite the distance between layers is 3.35 \AA .

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TABLE 1: QMD Energies per Atom Relative to Single-Plane Graphite ($E(\text{QMD})$), the Nuclear Volumes (V_n), the Van Der Waals (vdW) Volumes, the Inner Cavity Volumes, and the vdW Surface Areas for 65 Theoretical Fullerene Cages^a

fullerene		$E(\text{QMD})$, eV/atom	V_n , Å ³	vdW V , Å ³		inner V , Å ³		vdW S , Å ²	
n	sym			1.47	1.76	1.47	1.76	1.47	1.76
20	I_h^b	1.285	22.8	140.3	186.2	0.8	0.1	146.9	170.5
24	D_{6h}^b	1.146	31.5	168.4	220.7	1.6	0.2	169.2	193.6
26	D_{3h}^b	1.075	36.8	182.5	237.5	2.5	0.5	178.1	202.9
28	D_2	1.036	42.6	197.8	255.6	3.8	0.9	188.2	213.6
28	T_d^b	1.002	42.9	197.3	254.8	4.0	1.1	186.9	211.7
30	D_{5d}^b	0.993	46.4	210.7	271.6	4.0	0.9	198.1	224.3
30	$C_{2v(9)}$	1.002	48.3	211.9	272.3	5.2	1.6	197.0	222.7
30	$C_{2v(10)}$	0.937	48.9	212.7	273.1	5.5	1.8	197.0	222.3
32	D_{3h}	0.970	53.7	226.9	290.3	6.2	1.9	208.5	234.8
32	D_{3d}^b	0.944	52.3	225.5	289.2	5.4	1.5	207.9	234.7
32	D_2	0.928	52.7	225.8	289.3	5.7	1.7	207.6	234.1
32	C_2	0.913	53.2	225.9	289.3	5.9	1.9	206.8	233.0
32	D_3	0.855	55.0	227.6	290.8	7.0	2.6	206.4	231.9
40	T_d	0.747	80.9	288.9	362.9	14.2	6.6	244.3	271.1
40	D_{5d}	0.728	79.9	287.3	361.1	13.5	6.0	242.9	269.4
40	D_2	0.716	80.7	287.7	361.1	14.3	6.7	242.3	268.5
48	C_2	0.604	109.8	350.5	434.2	23.9	12.8	277.8	304.7
50	D_{5h}	0.556	117.2	366.0	452.3	26.4	14.4	285.6	312.8
60	C_{2v}	0.466	159.1	449.0	547.6	42.9	26.1	328.1	355.3
60	I_h^g	0.438	160.5	450.3	549.0	43.8	26.8	327.3	354.2
70	D_{5h}^c	0.395	204.6	535.5	646.3	62.2	40.0	370.3	397.6
72	D_{6d}	0.411	209.3	548.7	662.0	62.3	39.3	379.4	407.5
74	D_{3h}	0.390	224.1	570.5	685.7	71.1	47.0	386.3	413.4
76	T_d^b	0.391	234.5	589.0	706.8	76.1	50.7	394.5	421.7
76	D_2	0.384	230.8	585.8	703.3	73.0	47.9	395.2	422.9
78	D_{3h}	0.388	239.7	603.0	723.5	76.6	50.4	404.4	433.1
78	D_3	0.380	240.5	603.8	723.9	77.4	51.2	403.9	431.7
78	C_{2v}	0.378	241.4	604.3	724.4	78.1	51.9	403.5	431.4
78	D_{3h}^c	0.377	244.5	607.1	727.0	80.9	54.5	402.5	430.0
78	C_{2v}^c	0.374	243.1	605.8	725.8	79.6	53.3	403.1	430.2
80	I_h^b	0.387	255.6	626.2	748.6	86.4	58.7	410.8	437.6
80	D_{5h}^b	0.378	255.4	625.9	748.3	86.3	58.6	411.0	438.0
80	$C_{2v(22)}$	0.377	254.3	625.0	747.2	85.4	57.7	411.3	438.5
80	D_{5d}^c	0.377	248.3	620.6	743.4	80.0	52.8	413.5	441.5
80	D_2	0.377	249.7	621.2	743.6	81.4	54.2	412.3	440.3
80	$C_{2v(23)}$	0.376	252.7	623.5	746.1	83.9	56.4	411.8	439.0
84	$D_{2(11)}^g$	0.379	265.1	654.0	781.7	86.0	56.5	431.3	460.0
84	$C_{2(2)}$	0.369	267.4	655.1	782.5	88.4	58.9	429.7	457.9
84	$T_{d(20)}^g$	0.369	272.6	659.8	787.0	93.1	63.4	429.4	457.3
84	$D_{2(5)}$	0.359	270.5	657.7	784.9	91.3	61.7	428.8	456.4
84	$D_{6h(24)}^d$	0.357	275.2	662.6	789.7	95.1	65.2	429.4	456.7
84	$D_{2d(23)}$	0.353	275.3	662.0	789.0	95.6	65.8	428.0	455.1
84	$D_{2(22)}$	0.353	275.3	661.9	788.9	95.6	65.8	428.0	455.0
96	D_{6h}	0.335	331.2	766.7	908.1	119.3	82.9	479.2	507.0
96	D_{6d}^d	0.330	339.0	773.4	914.1	126.9	90.2	477.7	505.4
116	T_h	0.282	456.5	968.7	1132.6	189.2	140.8	557.1	583.9
120	D_{5d}^f	0.309	420.3	957.1	1128.8	149.0	101.7	583.5	615.8
120	$D_{5d}^{b,e}$	0.304	457.9	988.7	1158.0	181.6	131.8	575.0	603.4
120	$D_{5d}^{g,h}$	0.303	467.8	998.7	1167.2	189.4	138.6	577.7	605.7
120	D_{5h}^e	0.300	457.9	988.6	1157.9	181.6	131.8	575.0	603.3
120	D_2^g	0.290	472.9	1002.1	1170.3	195.0	144.3	574.5	602.6
120	D_{6d}^d	0.289	466.4	997.2	1166.5	188.8	138.1	576.5	605.2
120	D_6^f	0.288	482.2	1010.3	1178.2	203.4	152.4	573.6	599.9
120	T_d^g	0.282	470.5	1000.4	1169.1	192.5	142.1	574.7	603.0
126	D_3	0.276	510.0	1062.4	1237.3	215.5	161.1	597.5	625.5
130	D_{5h}^c	0.298	462.8	1040.3	1224.6	165.8	113.6	626.1	659.3
140	D_{5d}^f	0.292	505.7	1124.7	1321.0	182.9	125.6	669.0	703.1
140	D_5^e	0.278	557.3	1168.2	1361.0	227.4	166.7	656.6	686.1
140	I^b	0.245	617.5	1222.9	1412.8	281.8	218.3	651.3	676.1
144	D_{6d}^f	0.265	629.4	1251.1	1445.8	283.8	218.4	667.7	694.8
144	D_{6h}^f	0.258	629.3	1251.1	1445.6	283.7	218.2	667.8	694.2
144	C_{2^g}	0.248	629.8	1251.3	1445.8	284.2	218.8	667.3	694.4
150	D_{5h}^g	0.235	673.9	1317.9	1519.1	311.1	241.6	689.7	715.2
168	D_{6d}^f	0.238	776.1	1492.5	1714.7	362.9	282.6	763.1	790.1
180	D_{5d}^f	0.267	676.6	1459.8	1705.0	250.8	173.9	838.4	876.2
180	D_5^e	0.247	756.7	1528.0	1767.7	319.5	237.0	820.3	851.2
180	D_{6h}^d	0.235	775.9	1544.2	1782.7	336.8	253.2	818.2	849.5
180	D_5^c	0.203	906.9	1664.2	1897.0	456.9	367.8	803.1	826.5
180	I_h^g	0.201	907.8	1664.9	1897.8	457.6	368.5	802.9	826.7
228	D_{6h}^d	0.212	1024.4	1983.9	2278.2	455.8	345.5	1012.5	1045.7
228	D_2^g	0.175	1273.9	2212.4	2496.0	684.9	564.3	983.2	1004.9

TABLE 1: (Continued)

fullerene		$E(\text{QMD}), \text{eV/atom}$	$V_n, \text{\AA}^3$	vdW $V, \text{\AA}^3$		inner $V, \text{\AA}^3$		vdW $S, \text{\AA}^2$	
n	sym			1.47	1.76	1.47	1.76	1.47	1.76
228	T_d^8	0.170	1295.0	2233.1	2516.4	705.5	584.5	982.2	1003.3
240	I_h^8	0.158	1407.8	2389.7	2685.4	782.4	653.0	1025.8	1046.2

^a Each of the vdW volumes and surface areas is given for two extreme values for the vdW radius of the carbon atom, 1.47 and 1.76 Å. Subscripts in parentheses indicate the number of symmetrically distinct atoms for that isomer. For C_{84} , subscripts in brackets indicate the number of that isomer in the numbering scheme of Manolopoulos and Fowler.¹² ^b Includes Jahn–Teller distortion; hence, the symmetry name signifies topology only. ^c Capsule with C_{60} I_h caps. ^d Capsule with C_{72} D_{6d} caps. ^e Capsule with C_{80} I_h caps. ^f Capsule with C_{96} D_{6h} caps. ^g Made by the leapfrog technique.¹²

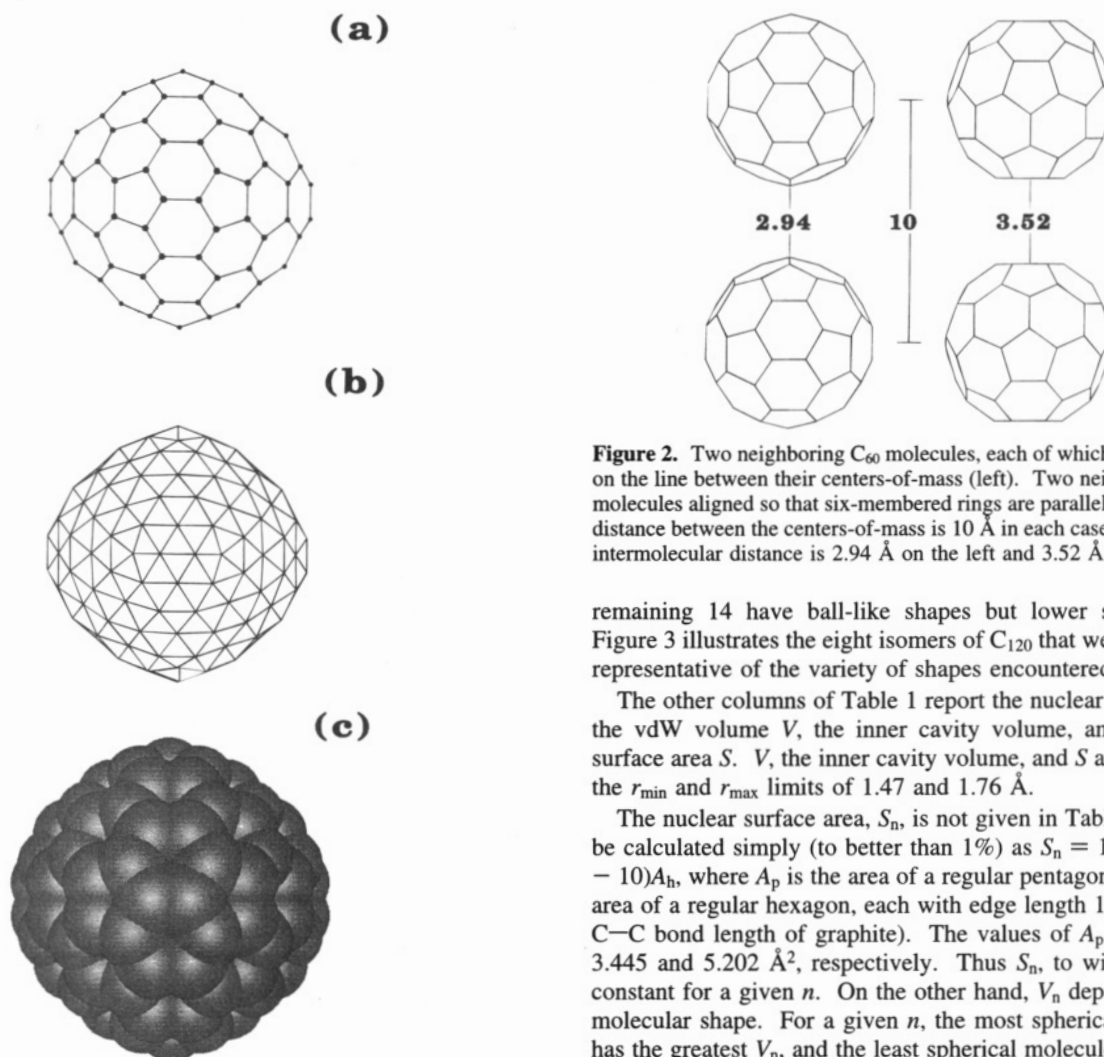


Figure 1. (a) The molecule $T_h C_{116}$. (b) Extra vertices placed at the centers-of-mass of the five- and six-membered rings, creating a set of triangles which are taken to define the molecular surface. (c) $T_h C_{116}$ with a vdW sphere of radius 1.47 Å placed at each atomic site.

Results and Discussion

The results of our calculations are summarized in Table 1. The first three columns of the table report the number of atoms n and the symmetry and the energy per atom as obtained by our first-principles QMD method for each of 65 fullerenes. The molecules studied include all possibilities with five- and six-membered rings for $20 \leq n \leq 32$ and six other molecules with $n < 60$. The remaining molecules all have isolated pentagons and include all possibilities for $60 \leq n \leq 80$, all icosahedral molecules for $n \leq 240$, and 34 others. The 34 others are of a variety of shapes and symmetries that were chosen with energy comparisons between various shapes in mind. They include 16 with capsular shapes and 4 with tetrahedral symmetry; the

Figure 2. Two neighboring C_{60} molecules, each of which has an atom on the line between their centers-of-mass (left). Two neighboring C_{60} molecules aligned so that six-membered rings are parallel (right). The distance between the centers-of-mass is 10 Å in each case; the shortest intermolecular distance is 2.94 Å on the left and 3.52 Å on the right.

remaining 14 have ball-like shapes but lower symmetries. Figure 3 illustrates the eight isomers of C_{120} that we studied, as representative of the variety of shapes encountered.

The other columns of Table 1 report the nuclear volume V_n , the vdW volume V , the inner cavity volume, and the vdW surface area S . V , the inner cavity volume, and S are given for the r_{\min} and r_{\max} limits of 1.47 and 1.76 Å.

The nuclear surface area, S_n , is not given in Table 1 but can be calculated simply (to better than 1%) as $S_n = 12A_p + (n/2 - 10)A_h$, where A_p is the area of a regular pentagon and A_h the area of a regular hexagon, each with edge length 1.415 Å (the C–C bond length of graphite). The values of A_p and A_h are 3.445 and 5.202 Å², respectively. Thus S_n , to within 1%, is constant for a given n . On the other hand, V_n depends on the molecular shape. For a given n , the most spherical molecule has the greatest V_n , and the least spherical molecule, such as a capsule-shaped molecule, has the smallest V_n . For example, for C_{120} , the most nearly spherical isomer has D_6 symmetry and a calculated V_n of 482.2 Å³, while the long thin capsular D_{5d} isomer with C_{60} -like caps has a calculated V_n of only 420.3 Å³. We also note that the most spherical molecules (the molecules with the greatest V_n) tend to be the lowest in energy, but that there are exceptions, such as in C_{120} , where the most spherical isomer has D_6 symmetry, while the lowest energy isomer has T_d symmetry. These exceptions tend to be the result of better electronic structure in the less spherical molecule; for example, $T_d C_{120}$ has a calculated HOMO–LUMO gap of 1.62 eV, while that for $D_6 C_{120}$ is only 0.51 eV.

The trends which hold for V_n and S_n are similar for V and S , but S is less constant than S_n ; in particular, long thin capsules such as $D_{5d} C_{120}$ tend to have a larger value of S than other isomers of the same n . This is because a more spherical fullerene has smaller average local curvature (greater average planarity). Higher local curvature, such as at the end of a

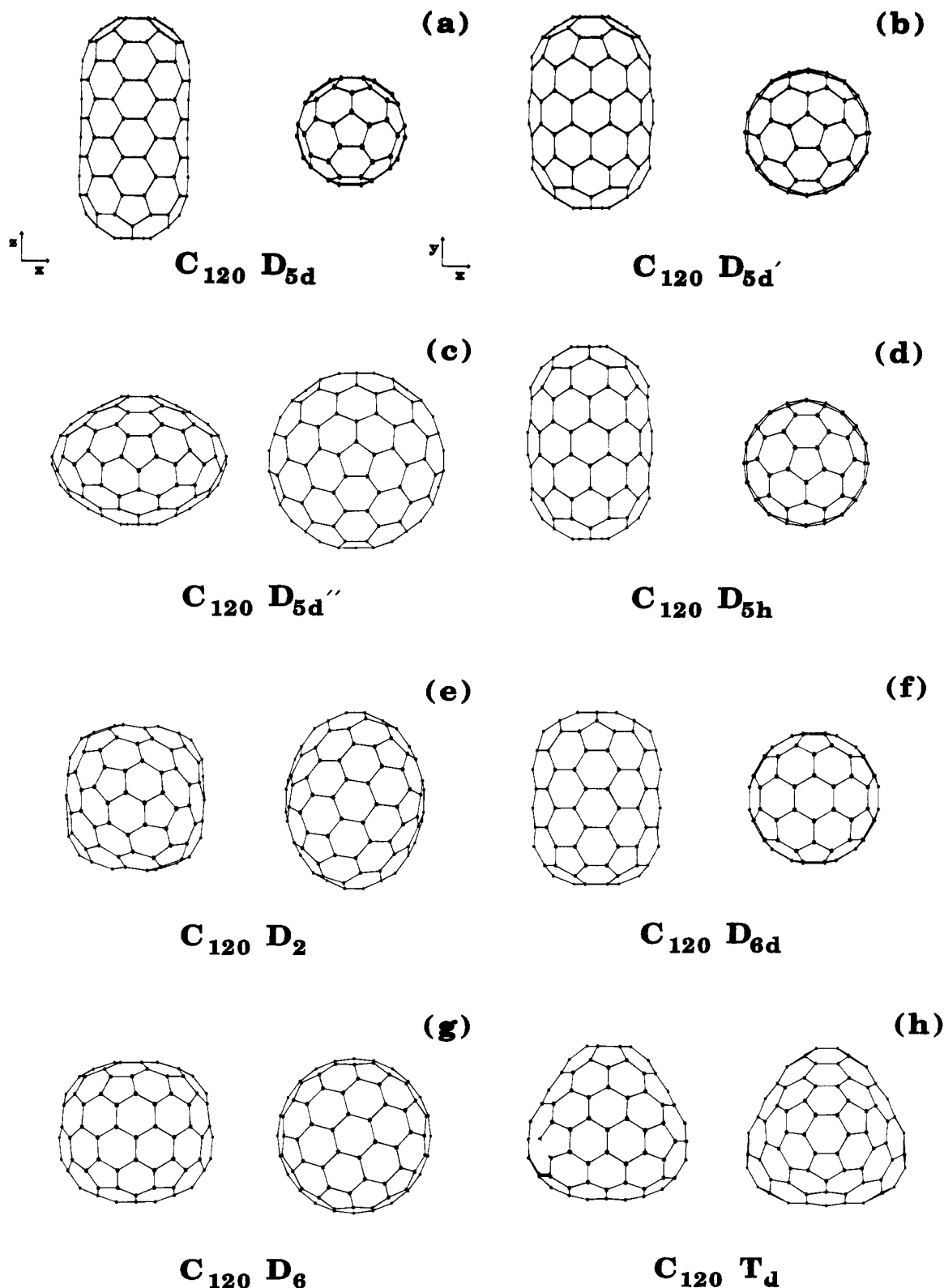


Figure 3. The eight C_{120} molecules considered in this work: (a) D_{5d} , a capsule with C_{60} caps; (b) D_{5d}' , a capsule with C_{80} caps; (c) D_{5d}'' , made by the leapfrog technique from D_{5d} C_{40} ; (d) D_{5h} ; (e) D_2 ; (f) D_{6d} ; (g) D_6 ; and (h) T_d . Side and top views are given, as defined by the axes shown in part a.

capsule-shaped molecule, means that more of the individual vdW spheres centered at each C are exposed to the outside. We also note that isomers with quite different shapes, such as D_{5d}'' , D_{6d} , and T_d C_{120} , can have similar values of V (or V_n) and S . This is because variations in these quantities, particularly of V_n , measure deviations from sphericity, and the deviation

may be quantitatively similar, whether the distortion is by squashing or stretching, or in a variety of symmetries.

In summary, we have calculated van der Waals surface areas (S) and volumes (V) and nuclear surface areas (S_n) and volumes (V_n) for a variety of C_n molecules with $20 \leq n \leq 240$. The coordinates used for the calculations are the result of first-

principles molecular dynamics relaxations. S_n can be calculated to within 1% by assuming that all bond lengths are 1.415 Å. We find that V_n is correlated with the energy of fullerenes with, for a given n , larger V_n generally corresponding to lower energy; but we point out exceptions to this rule. Our results for S and V will be useful in a variety of ways, especially in prediction or rationalization of fullerene solubility.

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