Molecular Free Surface: A Novel Method of Calculation and Its Uses in Conformational Studies and in Organic Crystal Chemistry

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Abstract: A simple but efficient method to compute the molecular free surface, S_M, as a sum of atomic free surfaces, S_{ai}, is proposed. A linear relationship is found between the number of valence electrons in the molecule and S_M. The atomic free surfaces can give information about the location of strain in the molecule. The molecular exposure ratio, or volume-to-surface ratio, is proposed as a parameter to describe molecular shape. A linear relationship exists between S_M and the packing energy of moderately polar organic substances. The atomic free surfaces are used to discuss the amount of cohesive energy provided by each single atom, and the tendency toward a constant energetic relevance of each atom in the crystal is discussed against the often wide differences in S_{ai}'s. The method lends itself to an easy extension for the calculation of effective free surfaces, such as are often considered in studies of the liquid state or of biological polymers.

Preliminary Remarks

Molecular structure determination today can be very accurate. Many diffraction or spectroscopic techniques produce molecular models in the form of a collection of Cartesian or internal coordinates describing the mutual positions of the nuclei. Most chemical uses of this information involve two fundamental quantities, the distance between bound atoms and the angles between bond vectors. Quite often, however, more complex functions of the atomic coordinates are used, like nonbonded distances or coordination spheres, or torsion angles, least-squares planes through some atom groups, and dihedral angles between these planes. Furthermore, certain comprehensive labels for molecular structure are sometimes introduced, like the T or G conformations in chain molecules, the propeller or antipropeller arrangement of polyphenyl compounds, or even such global parameters as for instance the pitch length in helical molecules of biological polymers.

One of the chemist's favorite arguments in molecular structure discussion is the steric factor, most often expressed as an admixture of all the above. The debate over its rigorous definition shows no sign of fading out, and yet its use in chemistry is pervasive, since it is a steady source of progress in rationalizing structure and understanding reactivity. Such a line of thought leads to the concept of molecular shape, a convenient definition of which calls in turn for a definition of atomic spheres.[1,2]

In this perspective there are other simple functions of atomic coordinates and radii that can be useful in the consideration of molecular statics and dynamics, as well as of intermolecular interactions. We have previously examined some chemical implications of molecular volume.[3,4] We wish to analyze here a novel and convenient definition of atomic and molecular free surface[5,6] and to sketch its applications to conformational problems and to the crystal chemistry of organic compounds.

Molecular Free Surface: Method of Calculation

Each atom i in the molecule is identified by a vector, $\mathbf{R}_{oi}$, in a given Cartesian reference system, and by a van der Waals radius, R_{vi}. The total atomic surface is then obviously that of the sphere centered at $\mathbf{R}_{oi}$ and with radius R_{vi}. This surface is sampled by a probe vector, in polar coordinates with origin at $\mathbf{R}_{oi}$ and $\rho = R_{vi}$, touching each point on the surface by a stepwise variation in θ and φ. The number of surface points that are found to be inside the sphere of any other atom of the molecule (or within a preset threshold distance, R_{th}, from it) are counted as N_{Ii}, while the other points are counted as N_{Oi}. The free atomic surface is then

$$S_{ai} = 4\pi R_{vi}^2 \frac{N_{Oi}}{N_{Ii} + N_{Oi}} \tag{1}$$

The total molecular free surface is then simply

$$S_M = \sum_{i=1}^{N} S_{ai} \tag{2}$$

where N is the total number of atoms in the molecule. The precision of the method depends somewhat on the total number of sample points; we have used a step of 2° or 3° in the polar coordinates θ and φ, resulting in 10300 or 4560 sample points, the differences never exceeding 1%. The overall error, as judged by comparison with the results from elementary geometry for test C_2 or C_7 aggregates, is 0.1 to 0.3%.

The one feature of this method which is quite novel, and crucial to further discussions, is that S_{ai} can be computed accurately and unambiguously for each atom in any molecular conformation. It will be found that this quantity depends (not unexpectedly) on the number of atoms in the coordination sphere, on bond angles and bond lengths, and on the number of short intramolecular nonbonded contacts, which reduce the free surface. Incidentally, it is this last effect that makes the calculation of S_{ai} by geometrical methods very hazardous. Under these premises, we may anticipate that S_{ai} and S_M can be used to gauge conformational effects, from which they depend very sensitively.
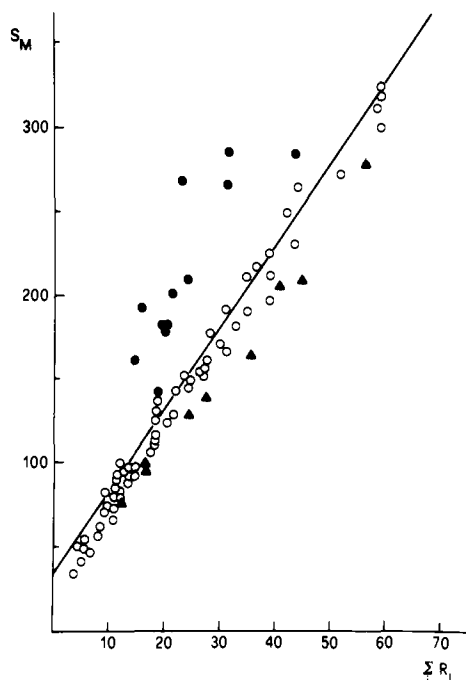
Molecular Free Surface: Results

For the purpose of making chemically significant generalizations, the free surface of many different organic molecules was computed. These included small molecules, such as methane, ammonia, carbon dioxide, methanes with oxygen- and nitrogen-containing substituents, mono- and polyhalogenated ethanes, a number of variously substituted benzenes and naphthalenes, a few heterocycles, and about 30 large molecules with up to 45 atoms.[7]

(1) On the derivation of atomic van der Waals radii from crystallographic information and on their relevance to organic crystal chemistry, see: (a) Kitaigorodski, A. I. "Molecular Crystals and Molecules"; Academic Press: New York, 1973, Chapter I. (b) Gavezzotti, A.; Simonetta, M. *Chem. Rev.* **1982**, *82*, 1.

(2) The ideal way in which molecular shape should be obtained is by some kind of quantum mechanical calculation. For instance, the work by Francl et al. (Francl, M. M.; Hout, R. F.; Hehre, W. J. *J. Am. Chem. Soc.* **1984**, *106*, 563) defines atomic spheres with adjustable radii by fitting a calculated electron density.

(3) Gavezzotti, A. *Nouv. J. Chim.* **1982**, *6*, 443.

(4) Gavezzotti, A. *J. Am. Chem. Soc.* **1983**, *105*, 5220.

(5) A previous method of calculation of molecular surfaces, by subtraction of intersecting caps from atomic spheres, is in the following: Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(6) Molecular free surface was analyzed for biopolymers by Finney (Finney, J. L. *J. Mol. Biol.* **1978**, *119*, 415). Due to molecular complexity, extensive use of effective radii for atom groups was made, ignoring single hydrogen atoms.

(7) A list of all molecules, with literature references and values for S_M, V_M, and packing energy, was deposited as supplementary material.

Molecular Free Surface

J. Am. Chem. Soc., Vol. 107, No. 4, 1985 963

Table I. Molecular Free Surface, S_M, Average Free Surface per Atom, $\bar{S}$, and Molecular Volume, V_M, for Some Organic Molecules

molecule	S_M, Å²	$\bar{S}$	V_M, Å³
methane	47.3	9.46	28.01
ethane	68.1	8.51	44.63
propane	89.6	8.15	61.39
n-decane	231.6	7.24	176.6
cyclopropane	78.8	8.76	42.70
cyclobutane	95.6	7.97	70.04
cyclohexane	126.9	7.05	99.20
adamantane	165.0	6.35	142.2
ethylene	61.6	10.3	40.25
acetylene	55.8	14.0	36.15
propene	82.2	9.13	56.72
benzene	107.4	8.95	85.40
naphthalene	154.1	8.56	128.8
azulene	155.4	8.63	129.2
biphenyl	183.3	8.33	157.1
water	33.5	11.2	16.82
methyl alcohol	56.9	9.48	34.89
acetone	90.9	9.09	62.86

Figure 2. A plot of molecular surface, S_M (Å²), against the number of valence electrons in the molecule. Black dots as in Figure 1. Hexaiodobenzene is denoted by an arrow.
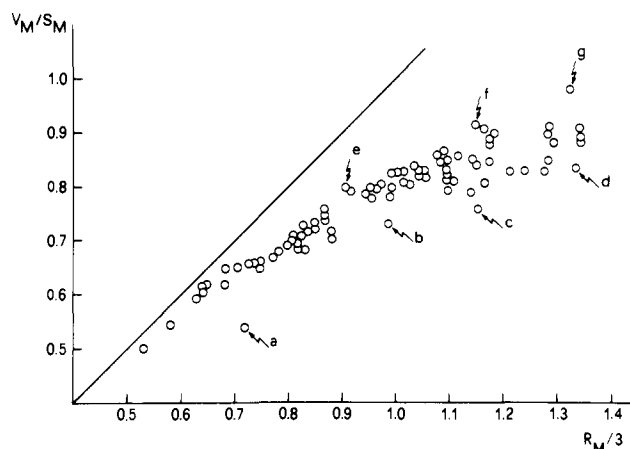
Figure 3. A plot of the exposure ratio, V_M/S_M, for molecules against the theoretical value for a sphere of radius $R_M = (3V_M/4\pi)^{1/3}$, $R_M/3$ (Å): (a) cyclopropane; (b) glycylglycine; (c) n-decane; (d) 1,4-butanediyldibenzoate; (e) benzene; (f) hexabromoethane; (g) hexaiodobenzene.

Figure 1. A plot of molecular surface, S_M (Å²), against the sum of van der Waals radii of atoms in the molecule (Å). Black dots refer to molecules with two or more Cl, Br, or I atoms. Triangles refer to cage or cyclic molecules.
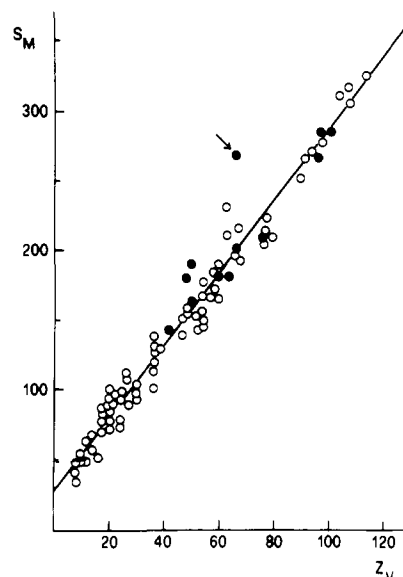
The geometrical parameters were taken from standard sources[8] for the smaller molecules and from X-ray crystal structure determinations for the larger ones, most of which were taken from a previously defined (and discussed) data set.[3] van der Waals radii were taken from previous work.[3,4] In all 85 molecules were considered, a population which is thought—on a somewhat arbitrary judgement—to include representatives from all the organic families, the only serious restriction being that no strongly polar or ionic bonds were present.

Table I shows some representative S_M values. What are the main variables determining the amount of free surface in a molecule? Obviously, the larger the molecule is the greater S_M is, and Figure 1 shows a plot of S_M against the sum of the atomic radii of all atoms in the molecule. The best straight line is

$$S_M = [4.883\ (0.233)][\sum_i R_{vi}] + [35.503\ (6.408)] \quad (3)$$

the quantities in parentheses being the standard deviations. For

24 molecules the discrepancy between observed and predicted S_M is larger than 20%. Compounds with large monocoordinate atoms, especially the higher halogens, exceed the S_M value predicted by the linear correlation, while the opposite is true for molecules with crowded centers, quaternary atoms, or molecules with cyclic and cage structures.

Figure 2 shows instead the plot of S_M against the number of valence electrons in the molecule, Z_V. The best straight line is now

$$S_M = [2.601\ (0.058)]Z_V + [28.13\ (3.16)] \quad (4)$$

and only 8 compounds deviate more than 20%. This is at the same time a new finding and a quantification of the internal consistency of the model, since a generally accepted view considers the van der Waals sphere as just an envelope of the outer electrons of an atom. In this context, the question of how much this envelope is distorted by the formation of chemical bonds is bound to remain without answer, since atomic surfaces are explicitly defined as rigid spheres and no attempt is made to interpret them in terms of actual electron distributions. Any predictive power of laws and formulas derived from such a position is, therefore, of an entirely empirical origin.

The volume-to-surface ratio, or exposure ratio (E_R), is larger for a convex body than for a concave one with the same surface.

(8) Bond lengths and angles were standardized to the values in Table I of Pople (Pople, J. A., Gordon, M. *J. Am. Chem. Soc.* 1967, *89*, 4253).

964   *J. Am. Chem. Soc., Vol. 107, No. 4, 1985*

Gavezzotti

Table II. Mean Atomic Free Surfaces (Å²) in Molecules (Dangling Bonds Are Saturated by C Atoms)

atom		S_a
X—H	hydrogen	
X = C		6.8
X = N		8.5
X = O		8.8
H_3—C—X	carbon	
X = C		13.0
X = N		15.9
X = O		15.1
H_2—C—X	carbon	
X = C		7.3
X = halogen		11.9 to 8.4
X = O		8.0
H—C<	carbon	4.1
—C—		1.0
H_2—C=	carbon	17.0
H—C=		11.0
>C—X	carbon	
X = C		5.9
X = N		7.0
X = O		8.0
X = halogen		9.5 to 5.6
H—C≡	carbon	21.2
—C≡		14.4
>C=O	carbon	
X = C		9.0
X = O, N		10.8
X = H		15.1
>C=O	oxygen	15.3
—N—H_2	nitrogen	9.5
—C≡N	nitrogen	17.8
—N—O_2	nitrogen	6.2
N—O	oxygen	15.4
—N<		2.5
—O—X	oxygen	
X = C		6.7
X = O		8.5
X = H		10.5

Table III. Average Group Increments for Molecular Free Surface Calculation (Å²) (All Dangling Bonds Are to C Atoms)

group	present work	ref 5	present − ref 5, %
—CH_3	33.4	35.2	−5
>CH_2	20.9	22.4	−7
>CH	10.9	9.46	+13
>C<	1.0	0.0	
=CH_2	30.6	30.9	−1
=CH—	17.8	17.9	+1
>C=	5.9	3.49	+41
		4.98	+16
—C_6H_5	94.9	88.5	+7
≡CH	27.8	28.9	−4
>C=O	22.3	26.6	−19
—NH_2	26.5	28.9	−9
—CN	32.2	36.4	−13
—NO_2	37.0	42.3	−14
—OH	19.3	24.2	−25
—COOH	43.4		
—CHO	35.2		
—F	12.1	18.3	−51
—Cl	29.0	29.9	−3
—Br	37.1	34.5	+7
—I	45.0	41.2	+8

$E_R = R/3$ for a sphere of radius R. For each molecule, the radius, R_M, of the sphere with volume V_M (the molecular volume) was computed, and $R_M/3$ was plotted against E_R. In such a plot, the spherical shape is therefore represented by a straight line. In Figure 3, one can see an increasing drift away from the spherical shape on increasing the molecular size, but some shape effects are also evident. Straight-chain molecules (linear alkanes, glycylglycine) have very low E_R's, while benzene, pyrazine, or even more so hexaiodobenzene and hexabromoethane have higher E_R's, given their globular shape.

The average free surface per atom

$$\bar{S} = S_M/N \qquad (5)$$

decreases as the hydrogen-to-carbon ratio increases in hydrocarbons (see Table I); this ratio being constant in saturated cyclic compounds, $\bar{S}$ decreases on increasing the total number of carbon atoms, since their coordination spheres are more evenly occupied as the ring size increases. In cyclohexane, $\bar{S}$ almost reaches the asymptotic value (7.5 Å²/atom) in polyethylene. Adamantane, with its closely knit cage structure, has the lowest $\bar{S}$ of all hydrocarbons. On the other hand, $\bar{S}$ sharply increases with unsaturation (see ethane, ethylene, acetylene, Table I). In general, the reciprocal of $\bar{S}$ is a measure of the saturation of atomic coordination spheres in a molecule.

Free Surface and Molecular Conformation

A careful survey of the S_{ai} values in sample compounds produced the average values shown in Table II, from which the average group increments of Table III were then derived. The choice was made on rather subjective grounds, including compounds judged to be "strain free" and with "standard" bond lengths and angles. We will take these reference values as basic parameters, since they claim neither derivation from or adherence to any first-principles theory of electronic structure.

The agreement with previous work[5] is generally good, and S_M can be considered as a model quantity that survives changes of parameters and method of calculation.
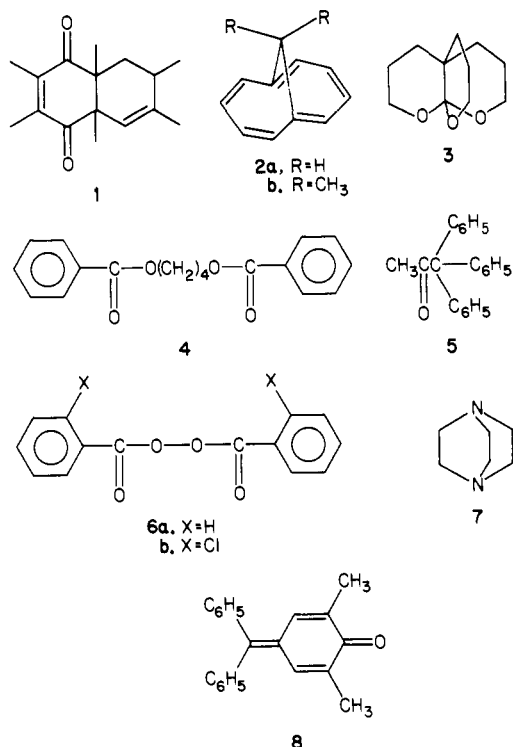
The data shown in Tables II and III neglect the influence of next-neighbor bonds, but this is partly justified by the small influence on S_M of small variations in bond lengths. On stretching the C=C bond of ethylene from 1.34 to 1.44 Å, for instance, the carbon S_{ai} changes by 0.6 Å², a change that would be quite negligible in a large molecule.

Surface group increments are more sensitive to conformational effects than molecular volume group increments.[4] If this sensitivity is a drawback when average values are looked for, it is by the same token just what makes atomic and molecular free surfaces useful in conformational problems. Deviations (on both sides) from the reference values indicate steric—or, more generally, structural—effects inducing strain at the atomic site under consideration. Bond stretching produces an increase in free area on the atoms pulled apart as does bond angle bending below the reference value. Steric crowding reduces the free area as a result of atomic spheres overlap.
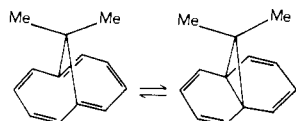
Unless—as is seldom the case—opposite effects cancel, a first evidence of strain in a molecule comes from a comparison between the S_M value as predicted by group increments and the value actually computed. A few examples, for some representative molecules, among which are the following, are collected in Table IV.

Linear, flexible molecules are essentially strain free, straight-chain alkanes being the obvious example. Cyclohexane also correctly appears to be strain free, and the result for adamantane is in agreement with the small strain energy of this molecule. The ring strain effect appears, as the ring size decreases in cycloalkanes, with an increase in free area with respect to reference. Strain is absent in biphenyl—thanks to rotation around the formally single bond—and in **4**, **6a**, and **6b**, where rotation around the appropriate bonds helps to accommodate even the bulky ortho-Cl substituents.

A smaller S_M than predicted by reference group increments is the result of overcrowding. In **2b**, the bridgehead atom suffers

Molecular Free Surface

J. Am. Chem. Soc., Vol. 107, No. 4, 1985 965

Table IV. Comparison between S_M Values As Obtained by Group or Atom Increments, Tables II and III (T), or from the Calculation for the Actual Molecule (C) ($Å^2$ Units)

compound	$S_M(T)$	$S_M(C)$	$(C - T)/T$, %
propane	87.7	89.6	+2
cyclopropane	62.7	78.8	+26
cyclobutane	83.6	95.6	+14
cyclohexane	125.4	126.9	+1
1	314.3	280.2	−11
adamantane	169.0	165.0	−2
2a	175.1	166.9	−5
2b	222.0	196.8	−11
biphenyl	189.9	183.3	−3
3	212.3	209.6	−1
4	331.4	328.0	−1
5	341.4	308.9	−10
6a	251.4	251.1	0
6b	285.6	286.5	0
7	130.4	138.3	+6
perchloronaphthalene	297.0	268.7	−10
hexaiodobenzene	303.0	269.7	−11
8	338.1	320.4	−5

from a decrease in free surface due to the formation of a trans-annular bond[9]

but some of the 12% decrement in free area arises from crowding of the methyl groups against the rings. Crowding is small in **8**, evident in **5** as well as in **1** (see below). The effects of ortho disubstitution are evident in hexaiodobenzene and perchloronaphthalene.

Figure 4 shows in a detailed fashion how the effects of crowding can be detected atom by atom. In **1**, the zone around the central C–C bond is crowded: methyl, methylene, quaternary, and vinyl carbon atoms have S_{ai} as low as 9.9, 4.8, 0.2, and 7.9 $Å^2$, respectively (compare with standards in Table II). Hydrogen atoms too show reductions of their S_{ai}'s down to 5.0 $Å^2$. In **5**, the S_{ai} of the benzenic C atoms facing another benzene ring show noticeable reductions.

From the above discussion, one can conclude that molecular and atomic free surfaces are a simple and immediate index of what is generally called a "steric hindrance", an index which can effectively and reliably replace a complex combination of many nonbonded distances or energies.

Free Surface and Packing Energy in Crystals

The van der Waals crystal packing energy, E, as computed by the usual lattice summations over nonbonded potentials, must depend very strictly on the number of valence electrons in a molecule. This point has already been discussed,[3] but the connection with packing energy was conveyed through molecular volume rather than molecular free surface, at that time not available. Figure 5 shows the relationship between S_M and E

$$E = [0.0767 \ (0.0034)]S_M + [1.448 \ (0.730)] \ \text{kcal/mol} \qquad (6)$$
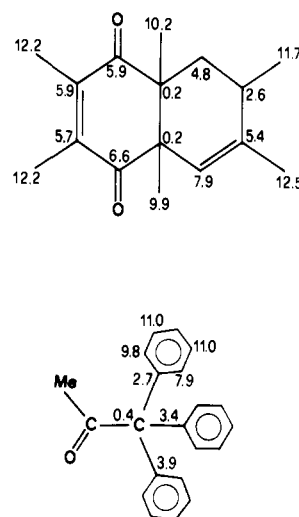
while the best straight line for the Z_V to E plot is

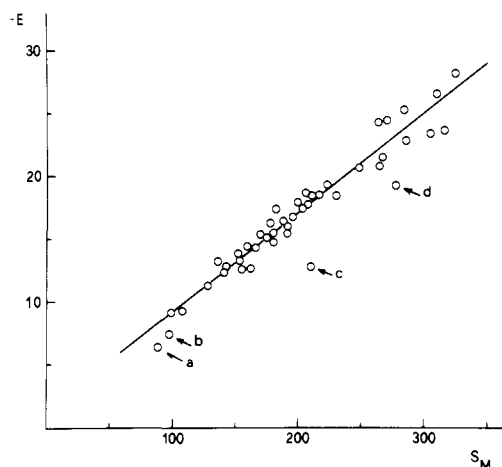$$E = [0.202 \ (0.012)]Z_V + [3.472 \ (0.815)] \ \text{kcal/mol} \qquad (7)$$

Through the use of (4), (6) and (7) can be seen to be fully

(9) Bianchi, R.; Morosi, G.; Mugnoli, A.; Simonetta, M. *Acta Crystallogr., Sect. B* **1973**, *29*, 1196.
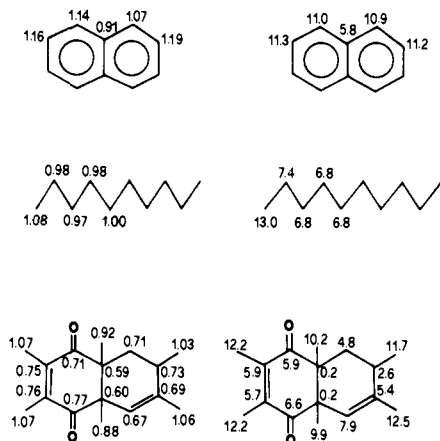

Figure 4. Atomic free surfaces ($Å^2$) in overcrowded molecules **1** and **5**.

Figure 5. Packing energy, E (calculated as in ref 3; at 7 Å cutoff; in kcal/mol) against the molecular free surface, S_M ($Å^2$): (a) furan; (b) pyrazine; (c) azobisisobutyronitrile; (d) **1**.

compatible. Only 8 compounds out of 45 deviate by more than 10% from (6); these can be mainly classified as involving electrostatic forces in the crystal. The cases of furan (−18%), **1** (−22%), and azobisisobutyronitrile (−36%) can be so explained, but it is still worth remembering that the term "electrostatic" does not necessarily refer to purely Coulombic forces, being in a broader sense a label for anything that was not included in the model at

966 *J. Am. Chem. Soc., Vol. 107, No. 4, 1985*

Gavezzotti

Figure 6. Energetic relevance (left; calculated as in ref 3; in kcal/mol) and free surface (right; Å^2) for atoms in the crystal of naphthalene, *n*-decane, and **1**.

Figure 7. Drop in free molecular surface on increasing R_{th} (Å) in the application of eq 1: (a) acetylene; (b) ethylene; and (c) ethane.

the time of the derivation of the nonbonded functions.

Besides the general effect shown in Figure 5, the atomic free surface has a subtler relationship with packing forces. In previous work,[3] the energetic relevance of an atom in a crystal, R_a, was defined as the portion of packing energy which is ascribable to that atom; and average R_a values were proposed for each atomic species. Roughly speaking, the more exposed atoms have larger R_a's, but there is not a simple proportionality between R_a and S_a. In fact, it is remarkable that an atom of a given species has about the same energetic relevance in all crystals—which means that crystals are built so as to allow each atom to come as close as possible to an average R_a; but it is even more remarkable that, as we find, the mean R_a tends to be achieved regardless of the type of atomic coordination. For instance, both a standard benzenic atom with $S_a = 11.0$ Å^2 and a standard methylenic C atom with $S_a = 7.7$ Å^2 show the same $R_a \sim 1.0$ kcal/mol; and a quaternary C atom with a surface of only 0.4 Å^2 reaches $R_a = 0.75$ kcal/mol. Thus, large or small exposure should not be judged on an absolute basis, but with respect to the reference values of Table II. An examination of Figure 6 is, on this point, self-explaining.

There appears in crystals—on the basis of the foregoing discussion—a certain segregation effect, by which molecules exposing non-H atoms in their outer surface have larger packing energies. To a higher level of accuracy, then, the packing energy depends to some extent on the nature of the exposed area. In an extreme example, naphthalene and *n*-hexane ($S_M = 154$ and 153 Å^2, respectively) have $E = 12.8$ and 10.9 kcal/mol, respectively, based on average atomic relevances;[3] the cohesive energy of the *n*-alkane is lower and pays a tribute to the scarce availability of its non-H atoms for intermolecular contacts. This can explain in part the difference in sublimation energies of the two compounds (15.7–19.6 and 12.15 kcal/mol, respectively[1a]).

We conclude this section by stating that, while the general relationship between S_M and E holds very well on the average for scarcely polar substances, a finer theory of the structure of organic crystals must take into account the effects of molecular conformation and of area segregation. We believe that the atomic and molecular free surfaces are a simple and convenient medium to describe such effects.

Contact Areas and Effective Areas

As defined here, the molecular free surface is a purely theoretical quantity and is quite different from the effective area available for intermolecular contact. For example, in many applications, it is more convenient to consider the surface spanned by the centroid of an object—e.g., a water molecule in the hydration sphere—in constant close contact with the molecule. This accessible surface provides a link with liquid-state properties; for example, it correlates very well with free energies of solvation or of solvent transfer.[10] In our methodology, this surface is obtained by appropriately increasing the van der Waals radii of atoms. As
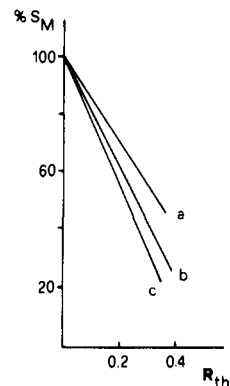
expected, the ratio of S_M to the accessible surface varies from 0.31 for methane to 0.45 for the flatter benzene molecule.

The contact area is, on the other hand, defined as that part of the molecular free surface that can be touched by a sphere rolling on that surface. We approximate this quantity by using $R_{th} \neq 0$ in the application of (1). Figure 7 shows the effects: atoms with large S_{ai} show a smaller drop in free surface than atoms with an already small S_{ai}.

Our method gives S_M values which are simply related to, or a multiple of, all the above effective areas. The following is an example of application in the field of biological polymers. The condensation of two glycine units gives the following balance[11]

$$2\text{glycine} \rightarrow \text{glycylglycine}$$

$$2 \times 95 \rightarrow 153 \text{ Å}^2$$
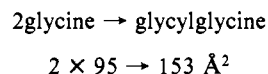
Rearranging gives

$$S_M(N) = 58.1N + 36.9 \text{ Å}^2 \tag{8}$$

for a polymer with N units. The protein surface is then computed by subtracting the contribution of a CH_2 group and adding the group contributions for CH plus the side chain—all this by appropriate use of Table III. This value is the reference one for a fully extended protein chain, without strain effects and H bonds. It is a relatively simple matter to obtain from it values for more biologically significant free areas.

Summary and Conclusion

It is possible, in a fast and reliable way, to evaluate the free surface of a molecule and to apportion it among its atoms. A table of standard surface increments for commonly occurring organic groups is established and can be used to calculate the free surface of any molecule.

The total free surface is found to be in linear dependence from the total number of valence electrons in the molecule, while the exposure ratio (volume-to-surface ratio) can be used to give a quantitative description of molecular shape. Future work may establish how this quantity can give insight into the properties of condensed phases—for instance, exposure ratio boundaries might be found for molecules producing liquid crystals.

Molecular and atomic free surface is found to contain some interesting information about molecular conformation and strain, and, in particular, the atomic values may be used to find the distribution of strain and crowding among molecular sites. A future development might be the quantification of this free area–strain energy relationship. But the atomic free area approach might be useful in cases where reactivity depends on steric factors at the reacting site.[12]

(10) Hermann, R. B. *J. Phys. Chem.* **1972**, *76*, 2754. Harris, M. J.; Higuchi, T.; Ryttins, J. H. *J. Phys. Chem.* **1973**, *77*, 2694. For the definitions of the various effective molecular surfaces, see also ref 6.

(11) The molecular structures of glycine and glycylglycine were both taken from the X-ray study of the second in Freeman et al. (Freeman, G. R.; Hearn, R. A.; Bugg, C. E. *Acta Crystallogr., Sect. B* **1972**, *28*, 2906) with few minor modifications.

The total free surface determines the crystal packing energy for moderately polar substances. A linear relationship is found between this energy and the free surface (or the total number of valence electrons). The relationship between packing forces and atomic free surfaces is a very important one. It appears that while the more exposed atoms have larger energetic relevances (that is, provide a larger amount of cohesive energy in crystals), the crystalline edifice is built so as to let any atom reach an average, constant atomic relevance. These arguments are, in fact, a (although partial) quantification of the close-packing principle: in the ideal close-packed crystal all atoms are exposed equally and have the same energetic relevance, corresponding to the maximum of intermolecular contacts in their coordination sphere. Future work along these lines may lead to a better understanding of crystal formation and growth.

A precise evaluation of molecular surface can be of great aid in studies of mutual molecular recognition, such as host–guest interactions in clathrates, or the reactant–substrate interplay in catalytic reactions (especially the biological ones). A natural extension of the method allows the computation of the free surface of biological polymers and its connection to effective or contact surfaces of biological interest.

Finally, it may be mentioned that the method can be adapted to give molecular area cross sections for studies of the deposition of monolayers on single-crystal metallic surfaces.[13]

(12) To give just two examples: (a) Adams, S. P.; Whitlock, H. W. *J. Am. Chem. Soc.* **1982**, *104*, 1602 (for the steric barrier to passage of arenes through the cavity of [8.8]paracyclophanes). (b) Seeman, J. I.; Viers, J. W.; Schug, J. C.; Stovall, M. D. *J. Am. Chem. Soc.* **1984**, *106*, 143 (for the dependence of reactivity to methylation in substituted pyridines from a geometrical accessibility factor at a crowded nitrogen atom).

(13) Gavezzotti, A.; Simonetta, M.; Van Hove, M. A.; Somorjai, G. A. *Surf. Sci.*, in press.

All the computer software needed to perform the surface calculations is incorporated in the OPEC program[3,4] and is available for distribution upon request.

Note Added in Proof. Further work and discussion have brought to the author's attention the following points: (a) the exposure ratio, E_R, should be renamed to shielding ratio, since it is a minimum for linear and a maximum for globular molecules; (b) comparison with Bondi's work[5] (Table III) is at some points obscured by a different apportioning scheme for >C= and by differences in the oxygen and fluorine van der Waals radii; (c) S_M and S_{ai}'s provide a useful guide to strain and accessibility at molecular sites, and their relationship to steric hindrance should be viewed in this light; (d) the S_{ai}'s can be used to calculate how much of the molecular surface is hydrophobic (coming from C, H) and how much is hydrophilic (coming from N, O), giving hints to intermolecular and solvation properties of the molecule; (e) heavily fluorinated compounds are found to deviate from the correlation of eq 7, since fluorine has many valence electrons under a small surface.

Photochemical Disproportionation of (MeCp)₂Mo₂(CO)₆ (MeCp = η⁵-CH₃C₅H₄) by Halides

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Abstract: The photochemical disproportionation of (MeCp)₂Mo₂(CO)₆ by halides in acetone, acetonitrile, or dimethyl sulfoxide proceeds according to the equation

$$(MeCp)_2Mo_2(CO)_6 + X^- \xrightarrow{h\nu} (MeCp)Mo(CO)_3X + (MeCp)Mo(CO)_3^-$$

The quantum yields for the disproportionation are dependent on the absorbed intensity of the exciting light but are independent of the concentration of X⁻. At low exciting light intensities, the quantum yields are greater than one. The following chain pathway is proposed to account for these observations: (1) (MeCp)₂Mo₂(CO)₆ ($h\nu,\phi$) → 2(MeCp)Mo(CO)₃; (2) (MeCp)Mo(CO)₃ + solvent → (MeCp)Mo(CO)₃(solvent); (3) (MeCp)Mo(CO)₃(solvent) + (MeCp)₂Mo₂(CO)₆ → (MeCp)Mo(CO)₃(solvent)⁺ + (MeCp)₂Mo₂(CO)₆⁻; (4) (MeCp)₂Mo₂(CO)₆⁻ → (MeCp)Mo(CO)₃⁻ + (MeCp)Mo(CO)₃; (5) (MeCp)Mo(CO)₃(solvent)⁺ + X⁻ → (MeCp)Mo(CO)₃X + solvent. The following results are consistent with this pathway: (1) (MeCp)₂Mo₂(CO)₆ will disproportionate in neat acetone, CH₃CN, or Me₂SO without added X⁻; (2) (MeCp)₂Mo₂(CO)₆ will not disproportionate in benzene containing added X⁻. Kinetic analysis of the mechanism reveals that the quantum yield for (MeCp)₂Mo₂(CO)₆ disappearance (Φ) will be linearly proportional to $I^{-1/2}$. This prediction was experimentally verified. In THF solvent, the quantum yield is dependent on the halide concentration. A mechanism involving direct reaction of the halide with the (MeCp)Mo(CO)₃ primary photoproduct is proposed. Analysis of the ligand concentration dependence data leads to a value of $\phi_{405} = 0.41$ in THF.

Recent papers have demonstrated the utility of studying the quantum yields of organometallic reactions as a function of exciting light intensity.[1-3] As part of our study of the photochemical disproportionation reactions of metal–metal bonded carbonyl

dimers,[4] we investigated the intensity dependence of the disproportionation of (MeCp)₂Mo₂(CO)₆ by halides (eq 1).[5] We report

$$(MeCp)_2Mo_2(CO)_6 + X^- \xrightarrow{h\nu}$$
$$(MeCp)Mo(CO)_3X + (MeCp)Mo(CO)_3^- \quad (1)$$
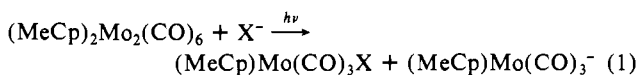
$$X = Cl, Br, I; \text{ solvent} = \text{acetone, Me}_2SO, CH_3CN$$

(1) Fox, A.; Poe, A. *J. Am. Chem. Soc.* **1980**, *102*, 2497–2499.
(2) Tyler, D. R. *J. Photochem.* **1982**, *20*, 101–106.
(3) Stiegman, A. E.; Tyler, D. R. *J. Photochem.* **1984**, *24*, 311–314.