Conclusion

From the present study it can be concluded that the AgO_2 molecule presents in fact two geometrical isomers of C_{2v} and C_s symmetry. Both structures correspond to the same potential energy surface and, from the energetic viewpoint, are only separated by about 0.4 kcal/mol, the C_s structure being the most stable.

The effect of the electron correlation on the calculated geometrical parameters of both forms is found to be considerable, although in this case the SCF and The CI description lead to the same conclusions.

Thus, from the theoretical study reported here, it can be concluded that the experimental results reported in ref 1–3 refers to a mixture of the two different forms of AgO_2. The small value of the ν_3 vibrational frequency indicates that the AgOO bending is almost free, and thus depending on the isolation technique, one or the other isomer will be found.

Cross-Sectional Areas of Alkanoic Acids. A Comparative Study Applying Fractal Theory of Adsorption and Considerations of Molecular Shape

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Abstract: Two independent novel theories are tested against each other by the determination of cross-sectional areas of a series of alkanoic acids: a recently developed method for the elucidation of molecular shape parameters; and fractal theory of adsorption. The numerical results obtained by the two approaches are virtually identical. It is concluded that the adsorption conformation of these acids on silica is horizontal. The two new approaches, which corroborate each other in this study, are described in detail, and a critical comparison to other methods for determination of molecular cross-sectional areas is made.

It is not very often that two completely independent theories, addressing the same problem, yield numerical results which are virtually identical. On one such case we wish to report here. The problem we address is the following. When a molecule is transferred from solution onto a (catalytic) surface it undergoes a drastic environmental change: the symmetry of its surrounding solvent cage is broken, and directionality, dictated by the molecule/surface interactions, is imposed. Consequently, one can attribute the molecule a specific conformation characteristic of the interactions which it experiences. Elucidation of these conformational parameters is not trivial. In the first section we briefly review some of the attempts to deal with the problem and point at the associated difficulties. We discuss two types of approach: through adsorption data and through parameters of molecular shape. In the second section we briefly describe two new theories, one for each of these two approaches, with special emphasis on how these theories offer improved answers to the conformational problems in question. The first is the fractal theory of adsorption[1-4] and the second is the theory of shape descriptors.[5-8]

In the third section we apply these theories to a series of *n*-alkanoic acids in interaction with the surface of silica; obtain complete agreement between results by the two theories; and from the mutual corroboration conclude on a flat-lying conformation. This conclusion is unusual in the sense that in most cases, soaplike molecules are attached, or said to be attached, to interfaces in a perpendicular manner. In the longstanding debate on this issue,[9-16] our results support those claiming a horizontal adsorption conformation in acid/silica interaction.

(I) Difficulties in Estimation of Molecular Cross-Sectional Areas

(1) Analyses of Adsorption Data. In 1936, Irving Langmuir wrote the following in a review:[17] "Today... I propose to tell you of a real two dimensional world in which phenomena occur that are analogous to those described in 'Flatland'.[18] I plan to tell you of the behavior of molecules and atoms that are held at the surfaces of... solids and liquids". The review was accordingly entitled "Two Dimensional Gases, Liquids and Solids". Surprisingly, this naive generalization, which is perhaps the privilege of pioneers only, has persisted widely until our time. The real world is not that of 'Flatland': the surfaces of most solids are

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convoluted, fractured, wiggly, and stepped.[19]

The rationale behind the most common method to calculate cross-sections of adsorbed molecules is the following: the surface area of a solid is measured by some standard technique, usually by the BET method,[20,21] using nitrogen as a probe molecule. The number of N_2 moles, n_1, forming a monolayer is obtained, and from the cross-sectional area, σ_1, of nitrogen (the commonly used value is $\sigma(N_2) = 0.162$ nm^2; see, however ref. 22), the surface area, A_1, is

$$A_1 = N_0 n_1 \sigma_1 \tag{1}$$

where N_0 is Avogadro's number. A monolayer value, n_2, of the molecule under investigation is determined, and the cross section σ_2 is calculated from

$$\sigma_2 = A_1/(n_2 N_0) \tag{2}$$

where the "flatland" assumption is actually hidden. This type of argument, which dates back to Livingston in the forties,[23,24] has been used extensively and is still used widely in various modifications in many modern studies.[25] In most cases, however, this approach is bound to lead to erroneous results: The use of eq 2 is limited to *flat* surfaces only, and these are not common. For most materials, the surface accessibility for a small molecule (e.g., N_2) is larger, sometimes much larger, than the surface accessibility for a large molecule (e.g., an organic adsorbate). This is simply due to the inability of the larger adsorbate to follow the fine geometric irregularity details of the adsorbent (for visualization of this argument, see Figure 1 in ref 26). In other words, we claim that σ values determined from eq 2 are overestimated; and indeed this is the case for the famous empirical equation of McClellan and Harnsberger (MH),[27] still cited widely in textbooks[28] and reviews.[29] This equation, which was based on a massive compilation of adsorption data (updated in ref 28), relates σ values calculated from liquid density values (see next section) to those obtained from adsorption, mainly through eq 2, for many compounds:

$$\sigma(\text{liq density}) = 6.16 + 0.596\sigma(\text{ads}) \tag{3}$$

This equation tells us that for typical adsorbates (tenths of nm^2 by either method), σ values from adsorption are "too large" compared to the simple liquid density model. Variations in packing factors are too small[30] to account for the prefactor 0.6 in eq 3. The reason is probably different. MH tried to formulate a "universal" equation in the sense that they took *all* surfaces they could find. Consequently, eq 3 represents some averaging process over all surface geometries, from flat ones (e.g., graphites) to extremely wiggly ones (e.g., porous silica gel), resulting in some average rough surface; and for such a surface eq 2 yields overestimated σ values, because of the limited accessibility considerations described above. In other words, behind each MH σ-value hides also all the irrelevant excess nitrogen (or argon) surface area.

By contrast, in the present study we arrive at the following result:

The cross-sectional area σ, as derived from data on the density of some liquids through analysis of molecular shape, is equal to σ as obtained by processing adsorption data.

In other words, our equivalent of eq 3 has a prefactor ~ 1 and a free term ~ 0. This result, of course, is for the specific series of compounds to be analyzed. The approach, however, is general.

To conclude this section, one has to mention that many workers were aware of the problem described here and tailored specific σ values to specific adsorption cases. Two representative examples are the studies of Koresh and Soffer on molecular sieves[30] and the re-evaluation of $\sigma(N_2)$ for adsorption on graphite.[31]

(2) Areas by Mensuration. Amoore introduced the practice of measuring cross-sectional areas on mechanical molecular models.[32] A scale model is constructed of the molecule, with atoms represented by spheres of appropriate van der Waals radii. Three silhouettes of the model, perpendicular to each other, are photographed and their areas determined. The three planes (xy, xz, yz) are defined as follows: axis x is the maximum length, z is the height at the minimum thickness, and y is approximately perpendicular to x and z. Variants of the construction have been used by other workers.[33-35] Very recently, the mechanical handling of models has been translated into a protocol for a computerized computation.[5-8] In this, the molecular shape is defined by atomic coordinates and atomic radii. Placement of the molecule in its principal coordinate system furnishes Amoore's three silhouettes as the sections in the principal planes xy, xz, and yz. Areas are estimated by superposing a grid and counting points within each section.

A computerized scan of a large number of molecules has shown that if van der Waals atomic radii are used, computed areas are frequently at variance with measurement.[7] Also, clearcut coincidences between measured and computed cross sections are not encountered. True, the range of experimental σ-values for a given compound is quite large[27] and, as discussed above, the plurality of surface types thwarts straightforward comparisons with computed numbers. It has therefore been proposed[7] that, for a preliminary orientation, a computed number be compared with the smallest among values measured at ambient temperature on an adsorbent of a low fractal dimension. Even so, pilot calculations for various compounds showed that the *largest* among the computed van der Waals cross sections falls short of the corresponding *smallest* measured value.

We have claimed above that the reported measured areas suffer from overestimation. We shall claim that numbers calculated for a molecule of van der Waals dimensions are inevitably underestimated. What one requires is a two-edged theory that simultaneously pulls adsorption numbers down and pushes computed numbers up.

(II) New Approaches

(1) Cross-Sectional Areas of Adsorbates from Fractal Analysis of Adsorption Data. The basis of this analysis is our finding that for the majority of adsorption data, a simple power law relates the apparent surface area, A, with the yardstick size used to determine it, i.e., with the cross-sectional area, σ, of the molecule used to coat the surface with a monolayer, n (mol of adsorbate/g of adsorbent)

$$A = N_0 n \sigma = k \sigma^{(2-D)/2} \tag{4}$$

$$n = k' \sigma^{-D/2} \tag{4a}$$

The fractal dimension,[36] D, which appears in the exponent of eq

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4 and 4a provides a quantitative indication of the degree of surface accessibility toward adsorption. The larger the D value, in the range $2 \leqslant D < 3$, the faster the accessible area drops with an increase in adsorbate size. The practice, interpretation, and uses of fractal theory of surface science have been discussed in great detail in recent publications.[1-4,26,37-48] Here we wish to emphasize one of the applications of this approach, that is, the ability to assess, directly from the adsorption experiment, the σ value, and from it the adsorption conformation. This can be done in two ways. The first (not used here, but demonstrated earlier[3,4,38,39]) employs the following type of argumentation: for a homologous series of adsorbates, used in a certain adsorption experiment, one assumes a common adsorption conformation and tests the data by eq 4. If a straight line is obtained on a log/log plot, and if its slope D is in the range $2 \leqslant D < 3$, one gets a preliminary indication that the conformational assumption is probably correct. To be certain, however, that the power law originates from purely geometric causes, as implied in eq 4, one adds data points obtained from a different adsorption experiment. Usually, the homologous set of compounds is adsorbed from solution, and the additional points are taken from a N_2-BET experiment. As an example we cite briefly our analysis of adsorption data of a series of polycyclic aromatic hydrocarbons from cyclohexane solution onto carbon black.[38] Only the assumption of a flat-lying conformation yielded good extrapolation to the N_2-BET point with $2 \leqslant D < 3$ ($D = 2.25$), i.e., surface geometric parameters seem to be dominant in that adsorption experiment. In a recent study, Pfeifer demonstrated that the adsorbent geometrical details are especially important in the case of adsorption of flexible polymers on a porous material,[39] even affecting greatly the thermodynamics of the system.

The second way to determine σ from fractal analysis (described in this Journal in a preliminary communication[1]) is more straightforward and is used below. The idea is to use eq 4 "backwards", i.e., to determine D independently, and then to measure n for the molecule under study. One can then calculate σ. We have applied this technique to the case of adsorbed n-alkanols on porous silica with average pore size of 6 nm.[1] The fractal dimension of this silica gel was established in numerous independent measurements as approaching the maximal possible value of 3 at scales not much larger than molecular scales. The physical meaning of such a high value is that the surface convolution is locally so high that adsorption sites are evenly distributed throughout the volume. The independent methods from which this high value was obtained were the following: small-angle X-ray scattering[40] following Schmidt et al.'s theory;[49] radiationless electronic energy transfer between adsorbed rhodamine B and malachite green,[40] following the theory of Blumen and Klafter;[50]
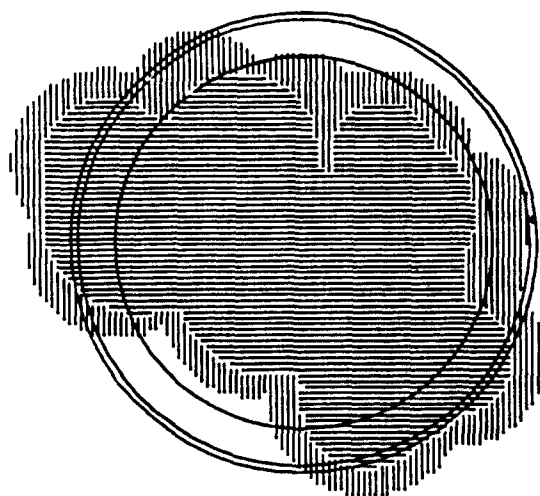

Figure 1. Cut through the asymmetric conformer of 2,2,4-trimethylpentane, showing van der Waals core (horizontal shading) and free volume (vertical shading). The cut is approximately in the average plane of the C_5-backbone, with the *tert*-butyl residue at the right. Circles represent spheres of volumes equal to the computed van der Waals volume; computed "reduced molecular" volume; molecular volume, as derived from the density at 20 °C (inner, middle, and outer circles, respectively).

analysis of surface area measured with a single probe, as a function of silica particle size;[1,3,40,41,43a] and application of eq 4.[37,40,51] Here we make special use of the last method, in the sense that we use eq 4 as a calibration curve. It was obtained by adsorption from solution of a series of branched spherical alcohols for which the σ value can be calculated with a fair degree of confidence (Figure 1 in ref 1). Recently, we have corroborated the calibration curve by showing that it extrapolates nicely to the N_2-BET value of the adsorbent.[40] The remarkable observation here is that geometrical considerations are sufficient to compare results from such different experiments as adsorption from solution and gas adsorption. Recent results of Drake et al. indicate indeed that if *chemi*sorption is involved, such comparisons and even determination of D become complicated.[51]

For the case of linear n-alkanols the interesting conclusion was reached, that the adsorbed alcohols cannot be represented by any of the classical pictures, i.e., neither as vertical rods with constant σ^{12} nor as spherical envelopes of all conformers, as calculated from liquid density.[27] Rather, they occupy prolate ellipsoids, which get more elongated with increase in chain length. The ratio between the two axes of the ellipsoid is not very large; even for 1-decanol it is only 2.1.[1]

(2) Estimation of Cross-Sectional Areas from Atomic Coordinates. The trouble with van der Waals atomic radii (r_w) is that they are geared to the concept of *minimal* contact distances.[52] The w solid, that is, the molecule as assembled from atoms of radii r_w, is consequently too small. Its volume (V_w) can account only for a fraction of the three-dimensional room (V_{mol}) that a molecule actually occupies in a condensed phase. The difference, $V_{mol} - V_w = V_f$, is said to represent an envelope of "free" or "void" volume that always encapsulates the w solid.[53,54] Put differently, V_f has to be invoked if one chooses to regard molecules as w solids. Obviously, the traditional choice of using r_w is not irrevocable: one can always use the molar volume as a guide to the molecular volume.[55,56]

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Figure 1 shows a cut through the asymmetric conformation (the more stable) of 2,2,4-trimethylpentane. This molecule was chosen for illustration because of its very irregular surface topography and large V_f. The inner shading delimits the w solid. By computation,[5] $V_w = 0.15$ nm^3/molecule. Yet, judging by liquid density at 20 °C (ρ), V_{mol} is almost twice as much: $V_{mol} = M/N_0\rho = 0.27$ nm^3/molecule. To stress the discrepancy, the inner and outer circles in Figure 1 are great circles of spheres of volumes 0.15 and 0.27 nm^3, respectively. In this case, the most extensive section through the w solid[7] amounts to 0.44 nm^2, while the smallest experimental estimate of σ is 0.54 nm^2.[27]

A way out is suggested by current approaches to a cognate problem, namely, computation of the volume of solute–cavities in solvents.[57] There, the practice is to protract the bond lengths beyond their covalent value[58] or replace r_w by multiples, e.g., substitute $1.7r_w$ or $2.5r_w$ for r_w of hydrogen.[57] In this spirit, we set to look for atomic radii that lead to molecular solids of volume close to V_{mol}. Details of the quest have been give elsewhere.[6] In brief, one distinguishes in a molecule the "core-atoms" (carbons of an alkane, carbons and hydroxylic oxygen of a carboxylic acid) from the "mantle-atoms" (mainly hydrogens). Since most of the core is deeply encased in the mantle, it is assumed that V_f is determined by the location and requirements of the mantle-atoms. The protracted radii of mantle-atoms can therefore be deduced by trial-and-error, such that computed volumes of various molecules be close to the corresponding V_{mol} values. We call the new radii "reduced molecular radii" (r_{rm}) and the volume they lead to the "reduced molecular volume" (V_{rm}). Since all molecules cannot be fit simultaneously by the same set of r_{rm} values, an additional constraint had to be imposed. We chose to make V_{mol} an upper bound to V_{rm} and put $r_{rm}(H)$ equal to a minimal value, 0.170 nm.[6] Even this minimal estimate is significantly larger than the van der Waals radius of hydrogen, 0.117 nm.[59] It is indeed well-known that $r_w(H)$ is too small to account for the volume requirements of hydrogen, neither in the intermolecular[30] nor in the intramolecular context.[60] In optimizing forcefield parameters, authors have in fact ended up with hydrogen radii as high as 0.15 (intra[61]), 0.158 (inter H···H[62]), and even[63] 0.182 nm.

For the reasoning behind our choice of a minimal value, consider Figure 1 again. The external shading adds V_f to V_w, inflating the computed volume from 0.15 to 0.25: quite close to, but still somewhat short of, $V_{mol} = 0.27$ nm^3/molecule. The middle circle is a cut through a sphere of volume 0.25 nm^3. Now, our context presents a complication that other investigators of molecular size[64–66] were not forced to face: we do not deal with the intricacies of an isolated molecule or of one solute-molecule in a sea of solvent. Rather, we have to refer to one molecule as a building-block of a bulk, e.g., of an adsorbed layer. The rm solid has therefore to guise as a unit-cell, repetitive translations of which fill the bulk up. Yet, construction from atomic radii leads inevitably to a well-defined shape which is not a parallelepiped. As the trace in Figure 1 shows, deviation from a shape appropriate to a unit cell is far from gross: the computed free volume (external shading) permeates crevices in the w solid (internal shading), smoothens them over, and renders bulges in the surface more similar in size to the dents; the volume that surface-bulging adds to the cell compensates roughly for the volume that dents detract; a bulge in one molecule would fit roughly a dent in its neighbor. Still, an approximation it is, and any attempt to build up a bulk from rm solids would unavoidably leave interstitial holes. Our intentional underestimation ($V_{rm} < V_{mol}$) is an admission that we cannot

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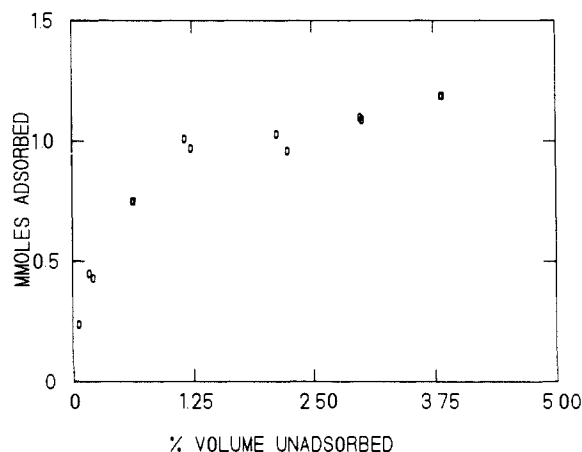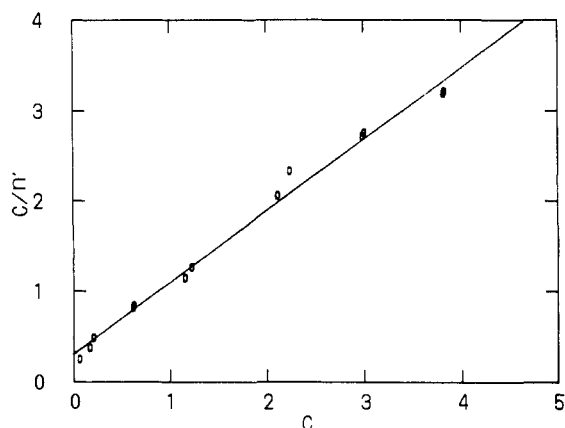(66) Allinger, N. L.; Hickey, M. J. *Tetrahedron* **1972**, *28*, 2157.

Figure 2. Adsorption isotherm of butanoic acid.

Table I. Monolayer Values and Cross-Sectional Areas for Aliphatic Carboxylic Acids on Silica Gel

acid	n (mmol/g)[a]	calcd (nm^2) from eq 6	1.d (nm^2)[b]
ethanoic	2.16 ± 0.01	0.285 ± 0.001	0.227
propanoic	1.47 ± 0.08	0.369 ± 0.015	0.271
butanoic	1.27 ± 0.02	0.407 ± 0.007	0.310
pentanoic	1.01 ± 0.02	0.475 ± 0.007	0.348
octanoic	0.85 ± 0.05	0.534 ± 0.021	0.448
nonanoic	0.63 ± 0.05	0.653 ± 0.035	0.478
dodecanoic	0.58 ± 0.02	0.690 ± 0.016	0.569
trans-2-pentenoic	0.94 ± 0.02	0.499 ± 0.001	0.332

[a] Best fit to eq 5. [b] Calculated from liquid density values, assuming sphericity.

estimate the volume of these holes. The heavily branched 2,2,4-trimethylpentane is an extreme case, where V_{rm} constitutes only 91% of V_{mol}. In the linear fatty acids to be discussed, mismatching is much reduced: the percentage is 94 (ethanoic) to 98 (nonanoic).

In the present context, V_{rm} is but an incidental tool that serves to estimate rm radii of mantle-atoms and to check the significance of computed numbers. Our main targets are σ values. These are obtained by a computerized version of Amoore's measurement of mechanical models.[32] As mentioned above and described in detail elsewhere,[7] the molecule is brought into its principal inertial coordinate-system, and the cross-section in each principal plane is mensurated. To this end, the planar section is subdivided into squares by a grid g. A scan is then conducted, square by square and atom by atom. If the middle of a square is within distance $r(X)$ of a center of any atom X, it is taken to contribute an increment g^2 to σ. Below, we report cross-sectional areas through rm bodies [$r(X) = r_{rm}(X)$] as well as through w bodies [$r(X) = r_w(X)$].

(3) **Estimation of Cross-Sectional Areas from Liquid Density Values.** By this commonly used method,[27] σ is calculated from liquid density values, under an assumption of sphericity of the molecules. The applicability and the limitations of this assumption were discussed in detail in ref 1 and will not be repeated here. Briefly, the assumption is correct for spheroidal molecules which are sufficiently rigid not to be distorted by the adsorption process.

(III) Experimental and Computational Results

(1) **Experimental Details.** The following materials were used: ethanoic acid (Frutarom), propanoic acid (BDH), butanoic acid (Fluka), pentanoic (valeric) acid, octanoic acid, nonaoic acid, dodecanoic (lauric) acid and *trans*-2-pentenoic acid (Aldrich), toluene (Baker Analytical grade), and silica gel (Woelm 63–200 μm, No. 04662, average pore size 6 nm, Lot No. 90 754/B). Solutions of acids in toluene were prepared in a concentration range of 0.5–6% (v/v). Adsorption experiments were carried as follows: dried (12 h, 180 °C, ~1 mmHg) silica gel was equilibrated with 5 mL of each solution for 10 min with constant

Figure 3. Langmuir plot of the adsorption isotherm of butanoic acid (C, % volume unadsorbed; n', mmoles adsorbed).

stirring. The slurry was then centrifuged, and the concentration of the unadsorbed acid was determined in the upper layer, from refraction index calibration plots. Refraction indices were determined at 30 °C with a Bellingham-Stanley refractometer, using a sodium lamp (589.6 nm).

(2) Results of Adsorption Experiments. The strong interactions between acids and silica surface make it appropriate to use Langmuir isotherms, i.e., multilayers are not built before completion of the first adsorption layer. Indeed, all acids obey nicely the Langmuir equation

$$\frac{C}{n'} = \frac{1}{bn} + \frac{C}{n} \tag{5}$$

where C is the concentration in the upper layer, n' is the amount adsorbed, n is the monolayer value, and b is a constant.

A typical adsorption isotherm and its analysis according to eq 5 are given in Figures 2 and 3. All monolayer values are collected in Table I, first column. Determination of the surface fractal dimension ($D = 2.97 \pm 0.02$) and derivation of the calibration curve for calculating σ value (eq 6) were described previously[1] (see also section II.1):

$$\log n = 2.50 - \frac{2.97}{2} \log \sigma \tag{6}$$

The second column in Table I contains the calculated σ value. For comparison, we bring in the third column σ value determined by the commonly used method[27] in which liquid density values are taken, and sphericity is assumed (section II.3). The gradual change of σ with increase in the number of chain carbon atoms is presented in Figure 4. Whereas in the case of adsorbed n-alkanols it was found that the sphericity assumption is an overestimation,[1] here we find that these values are an underestimation to the experimental results (Table I and Figure 4).

(3) Computational Details and Results. Mensuration of rm and w solids requires atomic coordinates as input. Since a well-tested molecular-mechanical force field for carboxylic acids is still not at hand, we recurred to experimental geometries, and also had to assemble some molecules from fragments. For ethanoic and propanoic acid, both electron-diffraction (ED)[67,68] and microwave data[69,70] are available. We used the ED data, because our value[6] of $r_{rm}(H)$ is based on geometries by the modified-MM1[71] and MM2[60] force fields, and these fields are geared to r_g bond lengths. The bonus is that ED coordinates are available for both the monomers and the dimers.[67,68] The extended conformations of butanoic and pentanoic acids were built up by appending a methyl
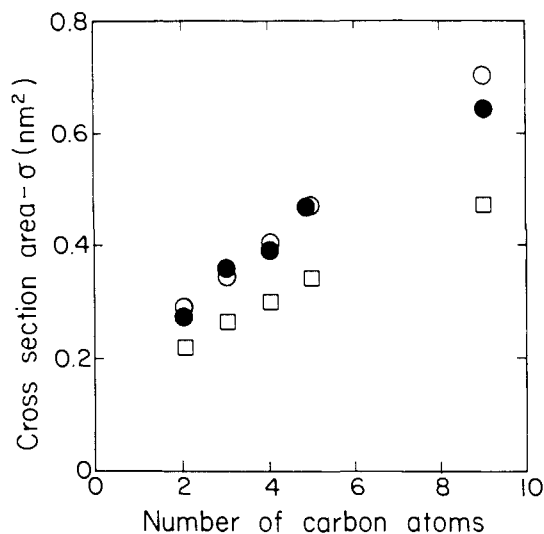

Figure 4. Cross-sectional areas of adsorbed alkanoic acids on silica gel: (O) computed; (●) from adsorption data; (□) from liquid density assuming sphericity.

Table II. The Volume of Carboxylic Acid Molecules[a]

acid	A ρ, exptl	B V_{mol}, exptl.	C V_{rm}	D V_{rm}	E ρ
ethanoic	1.0492	0.0950	0.0999	0.0941	1.0602
propanoic	0.9930	0.1239	0.1290	0.1238	0.9932
butanoic	0.9577	0.1528	0.1580	0.1528	0.9574
skew-butanoic			0.1548	0.1503	
pentanoic	0.9391	0.1806	0.1868	0.1816	0.9339
nonanoic	0.9055	0.2902	0.3009	0.2959	0.8881

[a] Acids are at the extended conformation unless stated. Volumes in nm^3/molecule. Column A: Measured densities ($\rho = D_4^{20}$) from literature.[74] Column B: $V_{mol} = M/N_o\rho$. Column C: Calculated for acidmonomers with the preliminary set of r_{rm} values. Column D: Calculated with the final set of r_{rm} values. Column E: Calculated from results in column D, $\rho = M/N_oV_{rm}$.

or an ethyl group to propanoic acid. The coordinates for skew butanoic acid were then derived by rigid rotation through 120° about C^2–C^3. Coordinates for nonanoic acid were obtained by appending a carboxyl group, shaped as in propanoic acid,[68] to MM2-optimized octane.

All the required van der Waals radii are known[59] (C, 0.175; H, 0.117; C=, 0.182;[72] –O–, 0.140; =O, 0.150 nm[73]). Of the rm radii, one has $r_{rm}(H)^6$ and still needs values for the carboxylic oxygen =O and for the lone electron-pairs, L, on the hydroxylic oxygen. In order not to bias the preliminary calculations, the two quantities were deduced independently by fitting to densities of compounds that do not contain a carboxyl. Densities[74] of neat alcohols at 20 °C indicate that the volume of lone-pairs can be ignored: $r_{rm}(H)$ by itself accounts fairly well for molar volumes. For example, with $r_{rm}(H) = 0.170$ and $r_{rm}(L) = 0$ nm, the computed V_{rm} of ethanol is 0.0954 nm^3/molecule (exo-conformation, optimized[75]) or 0.0946 (endo); from liquid density, V_{mol} is 0.0969 nm^3/molecule. Incidentally, alcohols at infinite dilution[76a] are fit by $r_{rm}(L) = 0.185$ nm. To obtain a first guess at $r_{rm}(=O)$, the computed V_{rm} of acetone (ecl-ecl conformation[66]) was fitted to the liquid-density value. This led to $r_{rm}(=O) = 0.213$ nm (V_{rm} = 0.122, V_{mol} = 0.122 nm^3/molecule). By using now the entire set of r_{rm}'s, V_{rm}'s were calculated for the acids. The outcoming numbers are compared with the experimental V_{mol} in columns B

(67) Derissen, J. L. *J. Mol. Struct.* **1971**, 7, 67.

(68) Derissen, J. L. *J. Mol. Struct.* **1971**, 7, 81.

(69) van Eijck, B. P.; van Ophensden, J.; van Schaik, M. M. M.; van Zoeren, E. *J. Mol. Spectrosc.* **1981**, 86, 465.

(70) (a) Stiefvater, O. L. *J. Chem. Phys.* **1975**, 62, 233. (b) Stiefvater, O. L. *J. Chem. Phys.* **1975**, 62, 244.

(71) Meyer, A. Y. *J. Mol. Struct.* **1977**, 40, 127.

(72) Estimated by raising Bondi's value (ref 73) to Gavezzotti's scale (ref 59).

(73) Bondi, A. *J. Phys. Chem.* **1964**, 68, 441.

(74) (a) Dreisbach, R. R. Ed. *Advances in Chemistry*; No. 29; American Chemical Society: Washington DC, 1961. (b) Weast, R. C.; Astle, M. J. Eds. *Handbook of Chemistry and Physics*; CRC: Boca Raton, FL, 1981.

(75) Meyer, A. Y. *J. Mol. Struct.* **1983**, 105, 143.

(76) (a) Kumaran, M. K.; Benson, G. C. *J. Chem. Thermodyn.* **1983**, 15, 245. (b) Badger, R. M.; Zumwalt, L. R. *J. Chem. Phys.* **1938**, 6, 711.
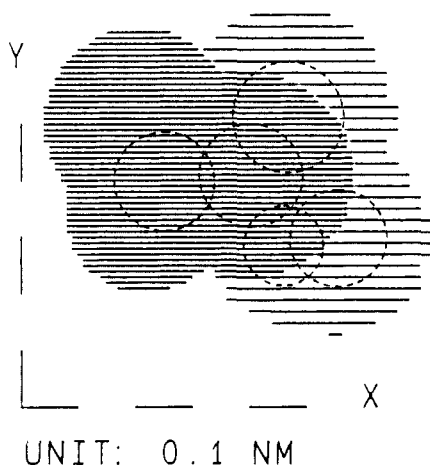
Figure 5. Cut through the first principal plane of ethanoic acid, distinguishing for clarity the alkyl segment (RC(=)–, dense hatching) from the hetero segment (OOH, sparse). In Figures 5–9, atomic circles (except alkyl hydrogens) are traced at half the given radii. Dashed circles, in plane of cut; solid, above plane; dotted, below plane. Lone electron pairs not shown.

and C of Table II. Coincidence with experiment is close enough to justify the procedure, but the ketonic oxygen is seen to be somewhat larger than a carboxylic =O. Adjustment of $r_{rm}(=O)$ to 0.195 nm, to fit propanoic acid exactly, leads to the pleasing numbers in column D.

A reservation may come to mind at this point. In estimating r_{rm} and in calculating V_{rm}, it is not feasible to take account of and weight appropriately all molecular species in the liquid. By contrast, the measured density and the corresponding V_{mol} are averages. If the computed cross section happens to be very close to a measured value, one would tend to conclude at most that the distribution of species in the adsorbed layer resembles the distribution in the liquid. However, as the examples in Table III show, the sensitivities of V_{rm} and σ to structural detail differ markedly. Stereochemical change affects V_{rm} only insignificantly; dimerization reduces it somewhat. σ values, however, are noticeably sensitive both to stereochemistry and to dimerization. It is therefore justified to calibrate the calculations by volumes and then use the computed cross sections as stereochemical probes.

Table IV presents now the results relevant to the Discussion, namely, areas of the three cross sections through rm solids. As already mentioned, each molecule was placed in the principal inertial coordinate system, such that $I_x > I_y > I_z$. σ_{xy} is therefore $\sigma_{rm,max}$. For the extended conformations, σ_{xy} passes through the skeletal plane and corresponds to the area excluded when the molecule "lies flat" on a surface; σ_{xz} passes along the skeleton but perpendicular to the skeletal plane, corresponding to the area excluded when the molecule "lies on its side". σ_{yz} is a cut through

Table III. Effect of Stereochemical Change and Dimerization[d]

species	V_{rm}	$\sigma_{rm,max}$
1. 2,2,4-trimethylpentane[a]		
asym conformation	0.2501	0.601
sym conformation	0.2518	0.570
2. ethanol[b]		
exo	0.0954	0.264
endo	0.0946	0.252
3. 3-chloro-2,3,3-trimethylbutane[c]		
stg	0.2328	0.403
ecl	0.2335	0.400
4. butanoic acid		
extended conformation	0.1528	0.417
C^2-C^3 skew	0.1503	0.433
5. ethanoic acid		
monomer	0.0941	0.301
dimer/2	0.0855	0.259
6. propanoic acid		
monomer	0.1238	0.360
dimer/2	0.1156	0.318

[a] Optimized by MM2.[60] [b] Optimized.[75] [c] Test-case suggested by Amoore's work[32] and optimized by us.[71] [d] V_{rm} in nm³/molecule, σ in nm²/molecule.

Table IV. Cross-Sectional Areas[a]

acid	σ_{xy}	σ_{xz}	σ_{yz}
ethanoic	0.301 (0.224)	0.227 (0.161)	0.155 (0.129)
ethanoic dimer	0.518 (0.421)	0.423 (0.322)	0.153 (0.077)
propanoic	0.360 (0.276)	0.296 (0.213)	0.226 (0.149)
propanoic dimer	0.636 (0.526)	0.457 (0.351)	0.164 (0.083)
butanoic	0.417 (0.328)	0.347 (0.252)	0.213 (0.126)
skew-butanoic	0.432 (0.317)	0.357 (0.258)	0.249 (0.167)
pentanoic	0.478 (0.379)	0.406 (0.297)	0.234 (0.139)
nonanoic	0.712 (0.582)	0.623 (0.467)	0.225 (0.131)

[a] Cross sections through rm solids and (in parentheses) w solid in nm²/molecule. Acids at the extended conformation unless stated.

the –CH_2–CH_2– chain, at the height of the center of mass. The latter section varies somewhat from one acid to another: it comes out smaller to the extent that the center happens to lie farther from a CH_2 group and closer to a midpoint of a C–C bond.

Computer-drawn cuts through the molecules are shown in Figures 5–9. Figure 6 (propanoic acid) stresses again the difference between V_w and V_{rm}. The two concentric circles are great circles of spheres of volumes equal to V_w (0.072 nm³) and to V_{rm} (0.129 nm³). The figures were traced by straightforward application of the Uniplot software, running the pen in parallel lines across the plane of section and making it draw when within distance $r_{rm}(X)$ of any atomic nucleus X. Variation in the density of shading distinguishes the alkyl segment ($CH_3\cdots\dot{C}=$) from the hetero segment (OOH).

Since the notion of an "rm solid" is new, one might wish to compare our numbers with the traditional van der Waals cross-
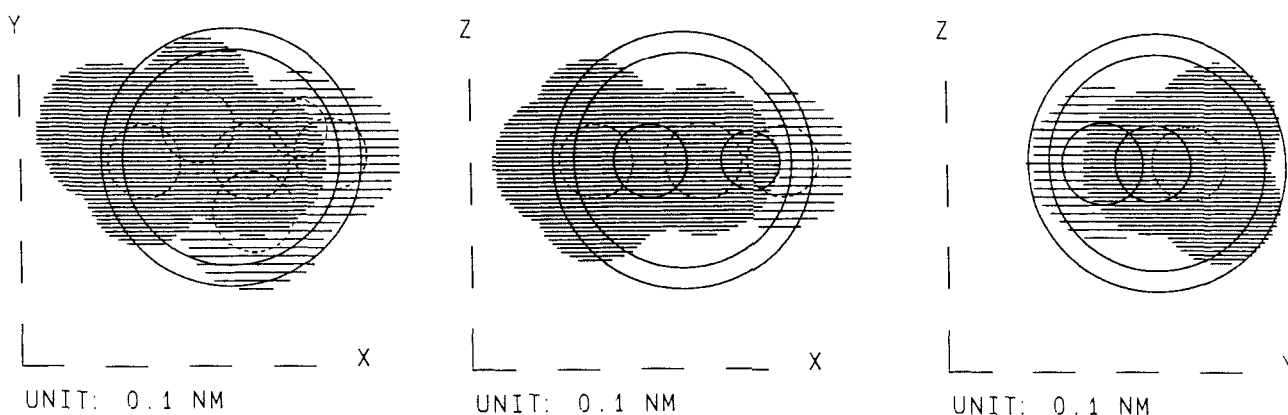

Figure 6. Cuts through the three principal planes of propanoic acid, corresponding to three conceivable modes of adsorption. Segments distinguished as in Figure 5. The large circles represent spheres of volume equal to computed van der Waals volume and to computed "reduced molecular" volume (coinciding in this case with measured molecular volume).
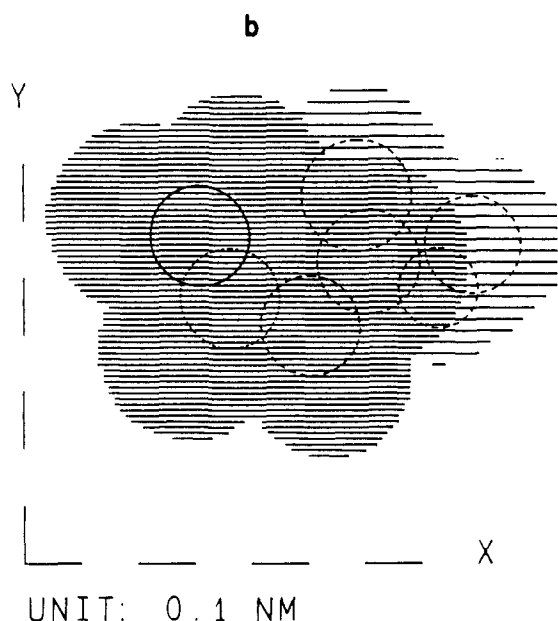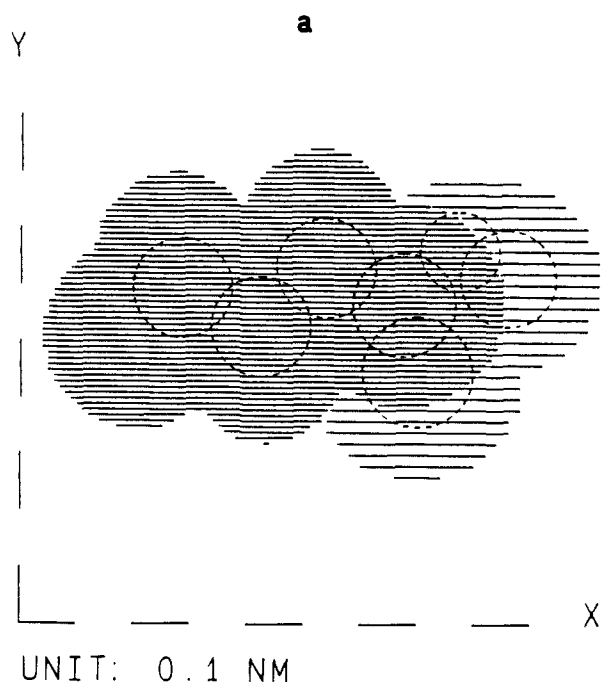
Cross-Sectional Areas of Alkanoic Acids

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a

UNIT: 0.1 NM

b

UNIT: 0.1 NM

Figure 7. Cut through the first principal plane of (a) the extended conformer and (b) the skew conformer of butanoic acid. Segments distinguished as in Figure 5. Carbonyl oxygen at bottom (a) and at top (b).

sectional areas. To this end, Table III contains also (in parentheses) the numbers computed for "w solids". It is immediately noticed that these constitute a gross underestimate. Most remarkably, σ_{yz} for the extended conformations (i.e., the thickness of an alkyl chain) comes out in the range 0.13–0.15 nm³/molecule. For comparison, Langmuir's classical value is 0.22[77] and the currently accepted range is 0.19–0.25 nm²/molecule.[35] Indeed, a process of "fitting" is required[35] in order to inflate the w solid to a reasonable size.

(4) Summary of Results. Comparison between the two methods is made for the short chain acids and for one of the longer chain acids (nonanoic acid). For ease of comparison we reproduce some
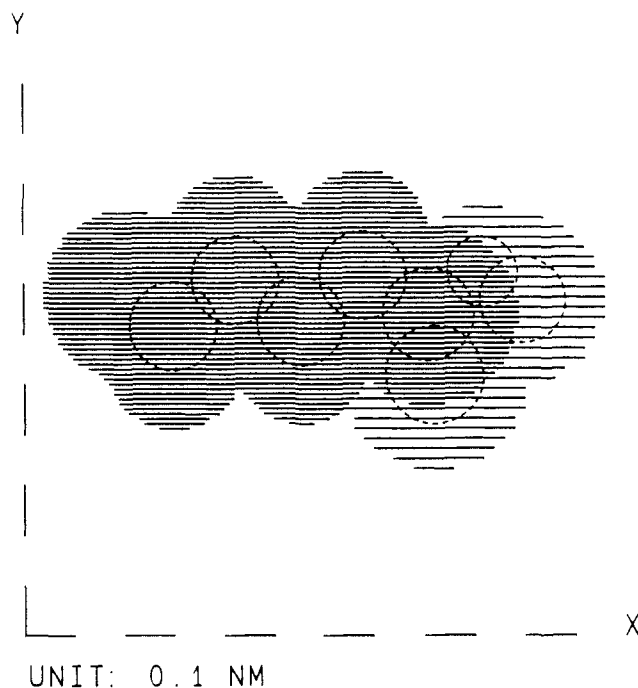
(77) Langmuir, I. *J. Am. Chem. Soc.* **1917**, *39*, 1848.

Figure 8. Extended conformation of pentanoic acid, stressing that even a C₅-chain is not yet long enough to be qualified as "rod-like". Asymmetry parameter,[76b] -0.97.
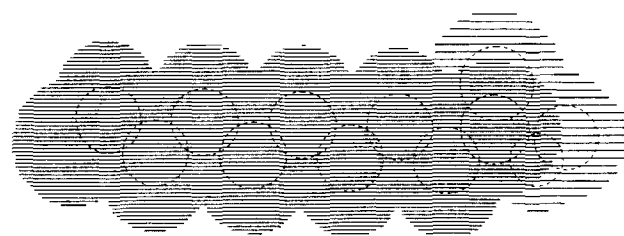

Figure 9. A truly "rod-like" molecule, the extended conformation of nonanoic acid. Cut through first principal plane. Asymmetry parameter,[76b] -1.00.

Table V. Comparison of the Fractal Approach and the Computational Method

acid	σ (nm²) (fractal theory)	σ (nm²) (computed)
ethanoic	0.285 ± 0.001	0.301
propanoic	0.369 ± 0.015	0.360
butanoic	0.407 ± 0.007	0.417
pentanoic	0.475 ± 0.007	0.478
nonanoic	0.653 ± 0.035	0.623

of the data in Table V and in Figure 4; the agreement is remarkable. The fine details are discussed below.

(IV) Discussion

The cross-sectional areas obtained for the acids are much larger than any of three indications for perpendicular adsorption conformation: (a) they are larger than the commonly accepted value of 0.205 nm²;[9,10] (b) they are larger than the cross-sectional areas of *n*-alkanols adsorbed on silica,[1] for which perpendicular adsorption was established;[1] (c) and they are much larger than the computed σ_{yz} values (Table IV). Furthermore, they increase with chain length, and they are even larger than the liquid-density spherical values. One must conclude therefore from the adsorption data that the acids are not adsorbed perpendicular to the surface. Indeed, the agreement with computation is clearly with σ_{xy}, i.e., the cross-sectional plane that passes the carboxyl atoms and a flat-lying alkyl residue. Although this result of parallel adsorption defies the common notion that soaplike molecules are adsorbed perpendicularly (as is indeed the case for acids adsorbed on water[9]), the same conclusion was reached in several early studies,
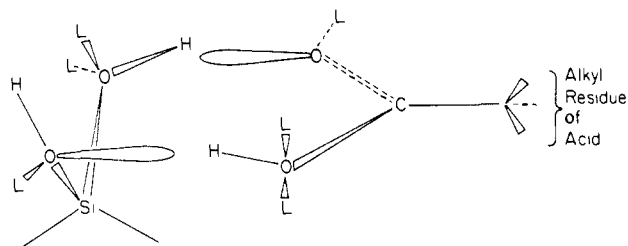
Figure 10. Bidentate adsorption of a carboxylic acid molecule by a geminal pair of surface hydroxyls. Letter L or a lobe denote the orientation of a lone electron pair on oxygen. Drawn from a model but still schematic.

Figure 11. Bidentate adsorption of a carboxylic acid molecule by a vicinal pair of surface hydroxyls. See legend to Figure 10.

even if sometimes by inaccurate arguments. Although these studies concentrated on fatty acids with chains much longer than in our study, discussion of their results is relevant and illuminating.

Claesson found in 1946 that "unbranched fatty acids were adsorbed on silica to the same degree when expressed in weight, regardless of chain length".[13] Since this means that the number of adsorbed moles decreases with chain length, he concluded on parallel adsorption. Today we known, however, that this is not necessarily the only conclusion: for *perpendicularly* adsorbed alcohols the number of adsorbed moles does decrease with chain length.[1] Brooks studied the adsorption of stearic (octadecanoic) acid on Aerosil[16] and used the N_2-BET in eq 2 to estimate σ. This is a case where the use of eq 2 is permissible, since Aerosil has a smooth nonporous surface with $D = 2.0$.[38] Brooks obtained σ = 0.650 nm^2 and from the very large deviation from 0.205 nm^2 concluded on parallel adsorption conformation. Kipling and Wright also studied the adsorption of stearic acid on silica.[14] Their value, 1.14 nm^2, was taken from adsorption on (flat) Graphon, applying eq 2. From this value they calculated the surface area of Cab-O-Sil (Aerosil) and of Microsil (precipitated silica). Despite the fact that their σ value is twice as large as Brooks' value, they claim that the ratio of observed to calculated monolayer on Aerosil is 1.0. That their σ is too high is also apparent from the value of 1.2 obtained for the above ratio on precipitated silica: for this porous material the observed surface area should be smaller than the calculated area since, as discussed in section I.1, the latter is overestimated by taking into account surface area accessible only to nitrogen. A possible source for the inflation of the σ value is its basis, i.e., adsorption on graphite. Adsorption on this surface is not entirely plane filling.[78] Kipling's overestimated value led Wu et al.,[15] who obtained from eq 2 a value of 0.80 nm^2 for linoleic (octadeca-9,12-dienoic) acid adsorbed on porous silica, to conclude that the acid molecules are adsorbed perpendicularly. To account for the fact that their σ value is still much larger than 0.205 nm^2 they suggest that not all available silanols actually serve as adsorption sites. Since they calculate a packing density of 1.25 molecules/nm^2, which is similar to the density of isolated silanols, they suggest that these are the adsorption sites. But again, their adsorption density is based on surface area which is inaccessible to the large acid molecules and therefore is greatly underestimated.[79] Another argument brought up by Wu et al. to support the perpendicular adsorption conformation is their finding that the number of adsorbed mol/g changes only slightly for five acids. However, since all chain lengths are in the limited range of C_{16}–C_{18} carbon atoms, this cannot be considered a strong argument.

We return now to our results and draw attention to a comparison made between pentanoic and 2-pentenoic acids. The interaction of π electrons with the surface of silica is stronger, by virtue of π-bonding with hydrogens, than the van der Waals interactions of alkanes with this surface;[80] a double bond provides an additional anchoring hook to the surface. Yet the two C_5-acids have very close σ values (Table I), suggesting that the saturated
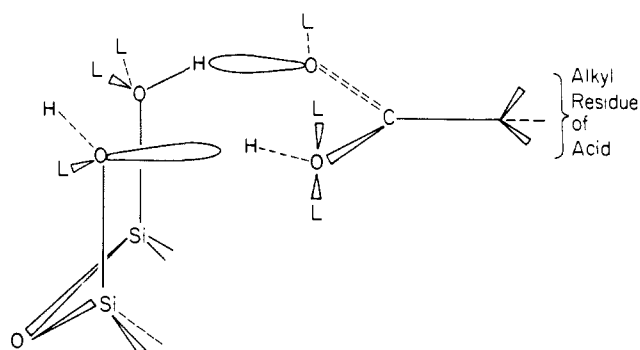
acid emulates the horizontal adsorption conformation of the unsaturated one.

Molecular models reveal no geometrical hindrance to horizontal adsorption (Figures 10 and 11). On the contrary, the carboxyl group, being bidentate, can use both the carbonyl-oxygen and the hydroxyl-hydrogen for hydrogen bonding to the surface.[81] The density of silanols on silica (4.5 Si-OH/nm^2)[10] is sufficiently high to provide hydrogen-bonding anchors to the two oxygens of the acid, either by geminal silanols or by vicinal ones as indicated also by Iler (p 656 in ref 10). The factors which enable side-way adsorption are two: first, the hybridization on the Si-OH oxygen, (sp^3), makes it possible to direct horizontally both the hydrogen and the nonbonding lone-pair electrons; and second, the best configuration for a hydrogen bond (i.e., the maximal energy gain) is when the X-H bond in one molecule and the lone pair orbital are aligned on the same axis.[81] Consequently, a ring is formed parallel to the surface, as illustrated in Figures 10 and 11. This situation is different from what is encountered for acids on water: in this case the chain is perpendicular due to the flexibility of the adsorbent (water) surface molecules which allows for a gradual side-chain lift-up as the pressure on the film increases.[9] The rigidity of silica allows some rotational adjustment around the Si-OH bond[82] but no more.

Another possibility which may be considered is that the acids are adsorbed on silica as dimers, as suggested by Kipling.[12] Kipling's argument was that silica surface is relatively nonpolar, and therefore it is not capable of breaking the dimer. The low polarity attributed to silica was taken from a heat-of-adsorption study by Zettlemoyer et al.[83] However, there is today overwhelming evidence to the contrary, mainly from spectroscopic studies of adsorbates.[84] The polarity of silica is estimated to be in between that of water and methanol. For instance, Leermakers et al. found a Z value of 88.[85] Such highly polar surface can break the dimers and induce monomeric adsorption, a conclusion reached by Iler as well (for C_6–C_{16} acids; p 656 in ref 10). Indeed, we find better agreement between the experimental σ values and the calculated monomeric σ values, compared to dimeric σ values (Tables III and IV). Several IR studies[86-88] indicate that the adsorption is usually monomeric and that "some" dimers adsorption occurs at high coverage. (Unfortunately, no quantitative estimation for this "some" is provided.) Our conclusion therefore is that monomeric adsorption is the favorable interpretation of

(78) Groszek, A. J. *Proc. R. Soc. London Ser. A* **1970**, *314*, 473.

(79) Incidentally, taking Wu's numbers, we obtained different values: ~0.90 nm^2 as σ of linoleic acid and 1.09 as adsorption density. These corrections, however, do not change Wu's argument.

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(81) Schuster, P.; Zundel, G.; Sandorfy, C. *The Hydrogen Bond*; North Holland: Amsterdam, 1976; Vol. 3.

(82) Levy, A.; Avnir, D.; Ottolenghi, M. *Chem. Phys. Lett.* **1985**, *121*, 233.

(83) Zettlemoyer, A. C.; Chessik, J. J.; Hollabaugh, C. M. *J. Phys. Chem.* **1958**, *62*, 489.

(84) (a) Avnir, D.; Levy, D.; Reisfeld, R. *J. Phys. Chem.* **1984**, *88*, 5956. (b) Leermakers, P. A.; Thomas, H. T.; Weiss, L. D.; James, F. C. *J. Am. Chem. Soc.* **1966**, *88*, 5075. (c) De Mayo, P.; Saforzadeh-Amiri, A.; King Wong, S. *Can. J. Chem.* **1984**, *62*, 1001.

(85) Evans, T. R.; Toth, A. F.; Leermakers, P. A. *J. Am. Chem. Soc.* **1967**, *89*, 5060.

(86) Hasegawa, M.; Low, M. J. D. *J. Colloid Interface Sci.* **1969**, *30*, 378.

(87) Marshall, K.; Rochester, C. H. *J. Chem. Soc., Faraday Trans. 1* **1975**, *71*, 1754.

(88) Marshall, K.; Rochester, C. H. *Faraday Discuss. Chem. Soc.* **1975**, *59*, 117.

our and others' data. However, we do not exclude the possibility that some dimeric adsorption occurs as well.

As to the conformation of the side chain, it seems to us that our conclusion reached for the side chains of adsorbed alcohols[1] is applicable here as well. We found that the term "linear" is misleading and that, in fact, the envelope of conformers is an ellipsoid with a surprisingly small ratio between the axes; for instance, in 1-butanol the deviation from a sphere is indeed small (an axes ratio of 1.2). For the acids in the present study, this is nicely illustrated in the computed silhouettes (Figures 5-9) from which it is evident that even the all-anti conformer is far from looking like a "straight narrow rod". Notice also the small variations in σ between the two conformers of butanoic acid (Tables III and IV and Figure 7). A contributing factor to the variety of the side chain adsorption conformations is the surface irregularity itself, which may force occasionally a skew-linkage on the energetically favored all-anti conformer. The "linearity" of the chain starts to show up only at relatively high lengths. Notice that the experimental value for nonanoic acid (Tables I and V and Figure 4) is somewhat smaller than the computed σ. This might reflect a partial lift-up of chains and chain overlapping as has been observed recently in an ESCA study of the adsorption of surfactants on silica.[89]

It should be stressed that our conclusions do not rest solely on the closeness of agreement between the processed experimental data and the numbers that a novel computational scheme provides. Comparison of measurement with van der Waals cross sections (Table III, numbers in parentheses) suffices, on qualitative grounds alone, to exclude the feasibility of perpendicular adsorption: the measured area changes too rapidly on going from one homologue to the next. The closeness of agreement is a result in itself, which we take to substantiate the proposed technique of estimating geometrical attributes of molecules. In practical terms, this means that it is not inappropriate to design molecular shape by using atomic coordinates and atomic radii, assigning relatively large radii to mantle-atoms. It seems indeed established nowadays that the

w solid is too small to represent a molecule, and that the larger volume obtained from liquid density (V_{mol}) provides a better approximation to size.[55,56] The pending question, apart from numerical detail, is not of volume but of shape: how should one mould the volume settled upon? Current choices are to enclose the w solid by a parallelepiped,[58] or build it up from "constant coordinate cavities" or combined fragments thereof,[90] or, alternatively, obtain the demarking surface through a quantum-chemical analysis of the charge cloud.[55] Our approach is simpler and more "chemical" than the latter choice; it may even turn out to be equivalent to it. Unlike the former options, the "reduced molecular shape" admits and preserves surface irregularities.

Coming finally back to the MH equation (eq 3), recall that our calculations also are of the "liquid-density type", but use densities only as a guide in deriving radii for mantle-atoms. Past this stage, and in dealing with specific molecules, measured densities are not referred to. It is the exploitation of shape that leads to the final estimates of cross-sectional areas. Within the bounds of error, both in measurement and in the theoretical estimate (coordinates, radii, grid method), they coincide with the experimental. Geometrical attributes of molecules have been calculated before but mainly as a tool to estimate or correlate derived quantities.[91] What we have provided here is a direct check of the attributes themselves.

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Formation and Structure of Molecular O=P-F. Mass Spectrometry, Infrared Spectra of the Matrix Isolated Species, and ab Initio Calculations[1a]

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Abstract: The molecules like SiF_2 and SO_2 are well characterized, but until now the isoelectronic compound OPF^2 has not been prepared. In the gas phase (10^{-2} mbar; 1100 K) this analogue of nitrosyl fluoride is formed by a reaction between $P(O)FBr_2$ and silver. This has been shown by mass spectrometric and matrix IR investigations (including $^{16}O/^{18}O$ shifts). By these experimental methods the following data have been obtained: $\Delta H°_{298} = -404.4$ kJ/mol, IP = 12.1 eV, $\nu(PO) = 1292.2$ cm^{-1}, $\nu(PF) = 811.4$ cm^{-1}, $\delta(OPF) = 416.0$ cm^{-1}, $\angle(OPF) = 109° \pm 5°$. The results of ab initio calculations are $R_e(PO) = 145$ pm, $R_e(PF) = 157$ pm, $\angle(OPF) = 110°$, 13a' MO = 12.8 eV (Koopmans). Data obtained for OPF are compared with those of the following isoelectronic molecules: SiF_2, SO_2, NSF, ONF, NOF.

The molecules OPCl,[3] OPBr,[4] SPCl,[5] OAsCl, and OSbCl,[6,7] which are similar to nitrosyl chloride, have been described very

recently. From a theoretical point of view these species are interesting as they link the long known dihalides of group IVa (14)[71]