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MODEL STUDIES OF CHEMISORPTION. INTERACTION BETWEEN ATOMIC HYDROGEN AND BERYLLIUM CLUSTERS

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ABSTRACT

The interaction between hydrogen atoms and Be metal clusters has been studied by *ab initio* electronic structure theory. Self-consistent-field (SCF) calculations have been carried out using both minimum and larger basis sets of contracted gaussian functions. Both spatially restricted and unrestricted SCF methods were used, and different results were obtained in several cases. Reasons for the choice of this particular model system are discussed. Clusters as large as 10 Be atoms have been considered, as have four different sites for the approach of the H atom. The electronic structure is discussed on the basis of predicted orbital energies and Mulliken atomic populations.

Introduction

One of the most challenging and important areas in experimental chemistry today is surface chemistry. However, it must be emphasized that surface chemistry is an experimental discipline. To illustrate this status quo we quote from Clark's recent book:[1] "How many surface atoms of the adsorbent participate in the bonding of a single adsorbed particle is a question that has not been answered unequivocally for any real system and probably will not be in the near future."

The difficulty with the above question is of course that it is the sort of conceptual question that is usually easier to answer from theory than experiment. Hence Clark's statement merely expresses the widely-held contention that theory is less than adequate, even at a qualitative level, for the problems facing surface chemists.

Our own opinion is that electronic structure theory is on the verge of becoming quite important for both surface chemistry and the less-clearly defined area of catalysis. To date this has been most abundantly shown in semi-empirical molecular orbital calculations of chemisorption. Perhaps the most noteworthy of these is an extended Hückel study by Anderson and Hoffmann[2] on the dissociative chemisorption of Li_2, B_2, C_2, N_2, CO, NO, O_2, and F_2 by nine-atom clusters of tungsten and nickel atoms. Using this simple method, Anderson and Hoffmann are able to correlate a large amount of experimental data, and in addition make several intriguing predictions. Finally, we note that their paper[2] gives a fairly complete bibliography of earlier semi-empirical studies of simple catalytic processes.

Perhaps the simplest example of catalysis is the fact that many diatomic molecules are known to dissociate on metal surfaces with little or no activation energy. The electronic structure aspects of this problem are two-fold: a) the two chemisorbed bond energies must be greater than the dissociation energy of the diatomic molecule in order for the process

$$A\text{-}A \quad + \quad \text{-M-M-} \quad \rightarrow \quad \begin{array}{c} A\ A \\ |\ \ | \\ \text{-M-M-} \end{array} \qquad (1)$$

to be exothermic; b) there must be a reaction pathway (by which the AA bond is broken and the $\overset{A}{\underset{M}{|}}$ bonds are formed) that does not involve a substantial barrier. It would appear that part a) of the problem, namely the understanding of a single chemisorptive bond, is the simpler half. Therefore in the present work, which is apparently the first <u>ab initio</u> study[3] of its type, we restrict ourselves to the attraction between a single hydrogen atom and a variety of clusters of beryllium atoms.

Choice of Be_n-H

Since, to our knowledge, the chemisorption of hydrogen by metallic beryllium has never been studied experimentally, one naturally wonders why this system was chosen. However, before answering that question, it should be made clear that experimentalists <u>will</u> be able to study this system should the theoretical studies prove interesting.[4] Therefore, at this stage, one should

not be unduly concerned about the lack of experiments with which to make direct comparison. Our reasons for choosing the Be_n-H system are basically four:

a) the Be atom has only four electrons. Actually, since a quantitative description of Be metal requires 2p orbitals, Be is not significantly less difficult to work with than B, C, N, O, or F. However, the latter five elements are not metallic.

b) the Be atom has a closed shell ^1S ground electronic state. Note that the first excited state ($1s^2\ 2s\ 2p\ ^3P$) lies at 2.72 eV.[5] Thus one hopes that the electronic structures of the atom and the metal will not be too drastically different, and that edge effects (due to the approximation of the metal as a finite cluster) will be minimized. This situation is to be contrasted with lithium metal, for which the unpaired spin of the atom could lead to difficulties with an <u>ab initio</u> cluster approach. We should point out that the extended Hückel method,[2] for example, does not suffer from this type of problem, since the total spin is never considered. However, a proper many-electron wave function will be an eigenfunction of $\underset{\sim}{S}^2$, and the assumption that a cluster of Be atoms has a closed shell ground state greatly simplifies our theoretical treatment.

c) the Hartree-Fock approximation is exceptionally accurate for the simplest Be_n-H system, namely diatomic BeH. The near-Hartree-Fock calculations of Cade and Huo[6] yield a dissociation energy D_e = 50.3 kcal/mole, compared with the experimental value recommended by Gaydon,[7] 56 ± 7 kcal/mole. Thus BeH is one of the very few diatomic molecules for which the Hartree-Fock dissociation energy lies within

the experimental error bars. Actually, however, D_e for BeH is known more accurately to be 48.8 ± 0.7 kcal/mole. The latter value comes from the exhaustive theoretical study of Bagus, Moser, Goethals, and Verhaegen.[8] Thus the Hartree-Fock dissociation energy of BeH differs from the exact D_e by only 1.5 ± 0.7 kcal/mole.

d) furthermore, as we shall see, even a minimum basis set (including $2p_x$, $2p_y$, and $2p_z$ functions on Be) yields a dissociation energy for BeH in close agreement with the exact result. Although one cannot guarantee that these fortuitously accurate BeH results will carry over to the cluster-hydrogen interactions, they are certainly a good omen.

Finally, we should note that there is at least one possible bad omen concerning the modeling of the H-(Be Metal) chemisorption using cluster models. That omen is the expectation that the electrons in metallic Be are relatively delocalized. This being the case, one might argue that the chemisorptive bond could be of a highly collective nature and require 100 or more surface atoms for a reasonable description.

Theoretical Details and Diatomic BeH

All of the results reported here have been extracted from single-configuration self-consistent-field (SCF) wave functions. A few calculations were carried out using two-configuration SCF methods, but the results were qualitatively similar. Two basis sets were used:

a) minimum basis set. Here 1s, 2s, $2p_x$, $2p_y$, and $2p_z$ functions on Be were used, while a single 1s function was centered on each hydrogen. Each function was a three-gaussian expansion[9] of a Slater function. Acutally, due to a transcription error, the 2s orbital differed slightly from that of Hehre, et. al.[9] The Slater function orbital exponents were those of Clementi and Raimondi:[10] ζ (1s) = 3.685, ζ (2s) = 0.956. Although the 2p orbital of the Be atom is not occupied in the electronic ground state, one can expect its spatial extent to be comparable to that of the 2s orbital, and hence we have used $\zeta = 0.956$ for the 2p orbital exponent. Finally, for the hydrogen atom, ζ (1s) = 1.15 was adopted. The atomic SCF energies obtained with this basis were -14.3919 hartrees (Be) and -0.4839 hartrees (H).

b) larger basis set. This basis is a contracted gaussian set of size Be (9s 2p/4s 2p), H (4s 1p/2s 1p). The beryllium primitive gaussian set of s functions was that of van Duijneveldt,[11] contracted 6111 to yield an SCF energy of -14.5704 hartrees, compared to the true Hartree-Fock energy,[12] -14.5730. The two Be 2p primitive gaussians, with exponents $\alpha = 0.509$ and 0.118, were taken from a previous study[13] of BeF_2. For the hydrogen atom, van Duijneveldt's primitive (4s) set was contracted 31 to (2s) and a scale factor of $\zeta = 1.2$ applied. For the H atom, this basis yields an energy of -0.4977 hartrees. Finally a set of 2p functions with exponent α = 1.0 was centered on hydrogen.

In summary then, our minimum basis set yields relatively poor total energies, while the larger basis appears to approach the true Hartree-Fock energies rather closely. The next logical addition to the basis would probably be a set of d functions on each Be atom.

However, this would probably have little qualitative effect on the results, while severely increasing computation time.

For some Be_nH systems rather different SCF results are obtained depending on the symmetry constraints imposed on the molecular orbitals. Therefore, the effect of such symmetry restrictions was investigated quite carefully in the present study. It should first be stated that each wave function represented a pure doublet (S = 1/2) spin state. Thus the restrictions to which we refer are of a spatial nature only.

Since the ground state electron configuration is by no means trivially obvious for several of the clusters, our initial calculations were performed with no restrictions imposed on the space orbitals. However, by studying the wave functions obtained in this way, it was possible in nearly all cases to determine the symmetry characteristics of the occupied orbitals. Given this information, spatially restricted SCF calculations were then performed. In the latter calculations, the open shell (or singly-occupied) orbital always transforms according to the totally symmetric irreducible representation. For all clusters, the restricted and unrestricted calculations give identical wave-functions and total energies with the H atom 50 bohrs away from the surface. This merely reflects the fact that the SCF solutions for the lowest singlet state of the isolated clusters are independent of symmetry restrictions. However, as we shall see in the discussion, for smaller Be_n-H separations, the imposition of a specific symmetry upon each orbital sometimes does raise the energy relative to the

spatially unrestricted result. In these cases, results were obtained using both restricted and unrestricted SCF methods. Such an energy difference is indicative of the qualitative importance of configuration interaction (CI), and it is perhaps best to use the unrestricted results when an energy lowering actually occurs. In the remainder of the text, we will in any case be referring to the unrestricted results unless specifically noted.

For diatomic BeH, our results are summarized in Table I. As mentioned earlier, both of our basis sets yield SCF dissociation energies within 10% of the exact value.[8] However, the larger basis set yields a bond distance 0.009Å longer than experiment, while the error using the minimum basis is significantly greater, 0.077 Å. Thus, as expected it seems quite likely that the larger basis set will yield the more reliable results for Be_n-H. However, by using both basis sets on the smaller clusters, we hope to be able to calibrate the minimum basis for our specific purpose.

The Smaller Clusters

For our purposes the "smaller clusters" are those for which both the minimum and larger basis sets have been used.

We should first indicate the assumed structure of the metal. Like the other alkaline earth metals, Be has a hexagonal close packed structure. The nearest neighbor distance a_o within a layer is 2.2866 Å; while c_o, the distance between similar (every other) layers is 3.5833 Å.[14] This means that the nearest neighbor distance between adjacent layers is 2.2255 Å. This rigid structure has been assumed for all of our Be_n clusters. In addition, chemisorption has been

considered only for the surface of highest symmetry, technically referred to as the (0001) surface.[15]

Our simplest cluster, equilateral Be_3, is seen in Figure 1. The only site we have considered for chemisorption is directly above the center of the triangle. This cluster may be labeled (3,0) to indicate that there are three atoms in the first layer and none in the second. The Be_3-H results are summarized in Table II. Note there that the distance r_e is the equilibrium perpendicular distance from the H atom to the plane of the (0001) surface. The dissociation energy is the difference between the energy of Be_3-H at r_e and that of Be_3-H with $r = \infty$. Since the single configuration (double spin state) wave functions for all such systems dissociate properly, there is no ambiguity concerning the procedure used to calculate the dissociation energy. For the Be_3-H case, the dissociation energy is rather small, 22 kcal/mole using the larger basis set. Since chemisorptive bond energy are typically(note however that the best experimental data are for transition metals) 60-70 kcal/mole,[1] it would appear that three Be atoms do a poor job of modeling the metal.

Two four-atom clusters have been considered. In the first, labeled (3,1), we simply add an atom to the second layer of the previously described Be_3 structure. This Be_4 cluster is seen in Figure 2. Again the site for chemisorption is directly above the center of the Be_3 triangle in the first layer. However, the structure of the metal is such that only every other three-fold site will be of this type. The others will <u>not</u> have a Be atom in this position in the second layer. To distinguish between the two

sites, we refer to that indicated in Figure 2 as the eclipsed site, since the H atom is directly above a Be atom in the second layer. The other site is in contrast called the open site. The second Be_4 cluster, seen in Figure 3, is a planar one, and its purpose is to model the bond midpoint site, a reasonably self-explanatory term.

The results for the two Be_4 clusters are also seen in Table II. The bond midpoint site leads to a much stronger chemisorptive bond than does the eclipsed site. However, it is also true that the near-tetrahedral[16] Be_4 structure lies significantly lower (68 kcal/mole) in total energy than does the planar model. In this regard it is especially interesting to note that near-tetrahedral Be_4 is predicted to be stable by 19 kcal/mole relative to 4 Be atoms. Since Be_2 appears[7] to be bound by less than 1 kcal/mole relative to 2 Be atoms, Be_4 might be the most stable species in the vapor of metallic beryllium. This point would appear worthy of a more detailed theoretical study.

Figure 4 illustrates the Be_5 cluster we have considered. This cluster is more interesting than the earlier ones, since each of the three previously described sites can be studied. This has been done and the results are given in Table III. There we note that both the minimum and larger basis sets predict the bond midpoint to be the most favorable chemisorption site. This is followed by the eclipsed site, with the open site being the least favorable. All three chemisorptive bond energies fall in the range 30-40 kcal/mole. In addition, it is interesting to note that the shortest distance from H atom to

(0001) surface occurs for the weakest chemisorptive bond. This is of course contrary to what is observed for ordinary chemical bonds.

Given the results of Tables II and III, we can draw some general conclusions concerning the adequacy of our minimum basis set. The first observation is that the minimum basis gives chemisorptive bond distances consistently longer than the more complete basis set. These bond distance differences range from 0.07 Å to 0.16 Å. Since this error is a) relatively small and b) fairly uniform, one can reasonably expect to predict chemisorbed molecular structures with reliability. The predicted dissociation energies are also in qualitative agreement with the results obtained with the larger basis set. Except for Be_4 (4,0), the minimum basis set bond energies are always less than those found with the larger basis. Thus, for the larger clusters, where only the minimum basis has been used, the true chemisorptive bond energies may be somewhat greater than the *ab initio* values.

The Larger Clusters

The discussion here will be broken down into sections describing the different chemisorption sites.

A. The Open Site, Figure 5 illustrates our first new open site model. It is a planar model, and, as seen in Table IV, a chemisorbed bond energy of 47.3 kcal/mole results. The difference between this and the Be_3 (3,0) result is particularly striking.

In the present approach, of course, one cannot assume a reliable model has been found until an increase in the size of the cluster does not qualitatively change the character of the chemisorptive bond.

Another model, Be_6 (3,3) is shown in Figure 6. There, three atoms have been added to the second layer of the metal. Interestingly, the chemisorptive bond energy, 55.3 kcal/mole, is roughly the same as that for the very different Be_6 (6,0) model. Comparing the (6,0) and (3,3) models with (3,0) indicates that the chemisorptive bond energy is greatly increased by enlarging the Be_3 cluster on either the surface or the layer immediately below. This being the case, one might naively expect the Be_9 (6,3) cluster (Figure 7) to bind a hydrogen atom by as much as 80 kcal/mole. However, Table IV shows that this is by no means the case, as the dissociation energy for Be_9-H is only 50.2 kcal/mole. Thus it is clear that the chemisorptive bond is <u>not</u> a sum of contributions from different atoms on the surface and below. In this sense the bonding is distinctly collective in nature. Although additional calculations would be necessary for a convincing demonstration, we are inclined to believe that Be_9 (6,3) does provide a qualitatively reasonable model for chemisorption on the open site of Be metal. If this is indeed the case, then we have given a partial answer to the conceptual question[1] discussed in the opening paragraph of this paper.

B. The Eclipsed Site. One additional model of the eclipsed site has been considered, namely that seen in Figure 8. This Be_7

model may be thought of as arising from the addition of three surface atoms to the near-tetrahedral Be_4 (Figure 2). Alternatively, one atom in the second layer has been added to the planar Be_6 model (Figure 5). The new Be_7-H calculations are summarized in Table V, along with the earlier minimum basis eclipsed site results. The binding energy of 40.8 kcal/mole is perhaps most directly comparable with the 47.3 kcal/mole found for the planar Be_6 model. This ordering is contrary to that based on the Be_5-H comparisons, where the eclipsed site is slightly more favorable than the open site for chemisorption. However, we tend to favor the Be_5-H comparisons, as it seems of the utmost importance to refer dissociation energy comparisons to the same Be_n + H dissociation limit. A definitive statement on the relative favoredness of the open and eclipsed sites will require consideration of a larger cluster. Even then, one may be forced to conclude that the two sites are comparable within the resolution (a few kcal/mole) of the theoretical methods available.

C. The Bond Midpoint Site. An additional planar Be_{10} cluster (Figure 9) has been used to model this third site. As seen in Table VI, a chemisorptive bond energy of 45.3 kcal/mole is predicted. Again, it is by no means certain that this bond energy is converged with respect to the number of atoms in the cluster. However, this Be_{10}-H result is consistent with the Be_5-H results in that the bond energy is greater (45.3 kcal/mole vs. 40.8 kcal/mole) than the largest model (Be_7-H) of the eclipsed site.

All three of the sites we have described thus far yield what Horiuti and Toya[17] have called "s states of chemisorbed hydrogen."

According to Horiuti and Toya, the s adatom is interstitially located between the electronic surface (perhaps defined in terms of <r> for the isolated metal atom) and the metal surface. They argue that s adatoms are less strongly bound to the surface the the more "conventional"

r adatoms. We have not yet considered r adatoms, which[16] "are situated outside the electron cloud of the adsorbent metal", and directly above one the metal surface atoms. In the rest of this paper then we will refer to the directly overhead site in the sense of the r adatom of Horiuti and Toya. We summarize then, their two qualitative predictions:

a) the directly overhead site should be more favorable for chemisorption than the open, eclipsed, or bond midpoint sites.

b) the perpendicular distance from the hydrogen to the metal surface should be longer for the directly overhead site than the three previously discussed sites.

With these ideas in mind, we proceed to the final model clusters.

D. The Directly Overhead Site. It is clear that the simplest model of this site is just diatomic BeH. The next model considered was that (Figure 10) in which a central Be has all six nearest neighbors on the surface. Table VII shows that the resulting Be_7-H bond is very strong, 71.3 kcal/mole. In fact this is the first model we have studied which yields a chemisorptive bond of strength comparable to that expected for the well-studied transition metals. In addition, the long bond length (1.43 Å) is consistent with the qualitative predictions of Horiuti and Toya[16] for an r adatom.

Unfortunately, the qualitatively satisfying results of the previous paragraph were not supported by the results for our largest model of the directly overhead site. In this model (Figure 11) three atoms in the layer immediately below the surface were added

to the Be_7 cluster described above. As seen in Table VII, the distance from the H atom to the metal surface is 1.43 Å, in essentially perfect agreement with both Be-H and Be_7-H. However, the binding energy is 27.3 kcal/mole, radically less than the 71.3 kcal/mole predicted for Be_7-H. Thus the rather abrupt and unexpected (from the other observed progressions) change in going from Be_7-H to Be_{10}-H makes it difficult at present to estimate the binding energy for the directly overhead site.

After some reflection, we have been able to conclude that the Be_7H model is not realistic. This conclusion is based on the observation that $Be_7(7,0)$ has a much smaller dissociation energy with respect to separated Be atoms. Specifically, the Be_7 dissociation energy is 25.5 kcal or 3.6 kcal/atom, while that for $Be_{10}(7,3)$ is 9.0 kcal/atom. Thus the Be_7 cluster sees the approaching H as a means of alleviating the "discomfort" brought on by its small dissociation energy.

As a further test, the Be_7H model was considered using a basis set intermediate between our minimum and larger sets. In this intermediate basis, the Be and H s functions were taken from our larger basis, while the Be p functions were from the minimum basis. The total energies obtained (e.g., -102.5542 hartrees at infinite Be_7-H separation) are of course much lower. However the equilibrium bond distance (2.681 bohrs = 1.42 Å) and chemisorbed bond energy (0.0995 hartree = 62.4 kcal/mole) are similar to the minimum basis results reported in Table VII.

Thus we see that the magnitude of the bond energy associated with the directly overhead site is not yet stabilized with respect to the number of atoms in the cluster. The final answer should be closer to 27.3 kcal than to 71.3, but additional studies will be necessary to further pin down this magnitude.

Electronic Structure Considerations

A great deal more information concerning the Be_n-H systems is given in Tables A through K. In particular, for each system studied are tabulated total energies, relative energies, orbital energies and Mulliken atomic populations. We wish to emphasize that our discussion of this data is not all-inclusive and in fact our primary goal is to stimulate further study of the data, the first of their kind.

The H atom orbital energy, approximately -0.5 hartrees, is in all cases much lower than the highest occupied orbital energy of Be_n. Thus one might expect an ionic $Be_n^+ - H^-$ electronic structure. However, as the Mulliken populations show, the H atom population remains near unity in essentially all cases. Thus we conclude that the chemisorbed bond is covalent in nature. Further, the singly-occupied orbital in the Be_n-H species is almost entirely composed of Be cluster orbitals. The H population of $\sim$ 1.0 occurs in the doubly occupied orbitals with orbital energy closer to -0.5 hartrees.

Tables A through E show that the minimum basis set orbital energies are very similar to those obtained using the more reliable larger basis

set. Thus we can expect the results for the larger clusters, where only the minimum basis was used, to be realistic. The Mulliken populations show a more obvious dependence on basis set. Specifically the Be 2p functions appear more important in the minimum basis picture. In the larger basis, of course, the s function space is much more nearly saturated, and the p functions can take on a somewhat more representative role. With either basis set, the Be 2p functions are seen to play a crucial role in the electronic structure. This is nearly as true for diatomic BeH as for the largest clusters considered. However, the magnitude of the p orbital contribution is best seen by a detailed inspection of the ground state electron configurations of several Be_n clusters. As an example, consider the planar $Be_{10}(10,0)$ cluster. If we construct molecular orbitals from ten Be atoms with $1s^2 2s^2$ orbital occupancy, then the molecular orbital occupancy is (valence electrons only)

$$\ldots\ldots\ 5a_g^2\ 4b_{3u}^2\ 3b_{2u}^2\ 6a_g^2\ 2b_{1g}^2\ 5b_{3u}^2\ 4b_{2u}^2\ 7a_g^2\ 6b_{3u}^2\ 8a_g^2 \qquad (2)$$

In fact, the lowest closed-shell electron configuration was found to be

$$\ldots\ldots\ 5a_g^2\ 4b_{3u}^2\ 3b_{2u}^2\ 6a_g^2\ 2b_{1g}^2\ 5b_{3u}^2\ 4b_{2u}^2\ 7a_g^2\ 3b_{1g}^2\ 1b_{1u}^2 \qquad (3)$$

Thus the Be 2p orbitals are of qualitative as well as quantitative significance, since the $3b_{1g}$ and $1b_{1u}$ orbitals cannot even be constructed from 1s and 2s functions on Be.

A similar unexpected result for $Be_7(7,0)$-H was pursued further using the intermediate sized basis described above, i.e., Be (9s 3p/4s 1p).

For this Be_7H system, the $1b_2$ orbital cannot be constructed from s orbitals on Be. However, our concern was that our minimum basis might favor the Be p functions in such a way as to predict an incorrect ground state electron configuration. This was our motivation for using the intermediate basis, which doubles the number of s functions. However, even this larger basis predicted the same electron configuration

$$\ldots\ldots\ 3a_1^2\ 2e_1^4\ 2e_2^4\ 1b_2^2\ 4a_1^2\ 5a_1 \qquad (4)$$

Thus we conclude that this qualitative importance of p functions is not a consequence solely of the minimum basis, but instead reflects reality.

Another interesting feature of several of the tables is the change in orbital energies where the spatially restricted and

unrestricted results differ. Usually, the correspondence between restricted and unrestricted orbitals is fairly clear. For example, in $Be_{10}(7,3)$ - H, the doubly-degenerate 4e orbital energy is -0.519 hartrees, while in the unrestricted calculation the nondegenerate 12a and 13a orbital energies are -0.522 and -0.519 hartrees. In the $Be_{10}(10,0)$ - H case, the unrestricted calculation yields a more uniformly spaced set of orbital energies. In the restricted calculation, the three highest ε values are -0.249, -0.240, and -0.176 hartrees, while the unrestricted results are -0.248, -0.233, and -0.227 hartrees.

Although the calculations provide a number of other interesting predictions, we will discuss only one more, the electron distribution in the $Be_{10}(7,3)$ - H system, Figure 11 and Table K. Note first that in the isolated cluster, the three unique atoms have populations 3.97 (six of these), 4.05 (three) and 4.00 (one Be atom). Thus the electron distribution is relatively uniform amongst the ten atoms. However, in going to Be_{10}-H, both restricted and unrestricted treatments show a population of 4.4 electrons on the unique central atom. Roughly 30% of this marked increase in electron density is due to the H atom, which is positively charged in this simple picture. However, a larger contribution comes from the six Be atoms on the same layer. Note that the same general trend is seen in the $Be_7(7,0)$ - H model results. Thus it would appear that for r-site chemisorption, a substantial increase in electron density occurs at the metal atom closest to the adsorbed hydrogen.

Conclusion

The chemisorption of atomic hydrogen has been studied using clusters as large as ten Be atoms. Our tentative conclusion is that a ten atom cluster is just about adequate for modeling chemisorption. However, future studies of larger clusters will be necessary to firmly establish this hypothesis. Three of the sites studied--the open, eclipsed, and bond midpoint sites--are comparable with respect to chemisorbed bond energy, $\sim$ 40 kcal/mole. The directly overhead site remains more uncertain, with the largest cluster studied yielding a bond energy close to 30 kcal/mole. A wealth of qualitative information has been provided concerning the electronic structures of both the Be_n clusters and the composite Be_nH systems. At this point, experimental studies of the chemisorption of H atoms by metallic beryllium would appear in order and in fact be welcomed.

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16. This Be_4 cluster is not a true tetrahedron, since the distance to the Be atom in the second layer is 2.2255 Å. The three surface atoms, however, lie 2.2866 Å apart.

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TABLE I. Theoretical results for the BeH molecule.

Method	r_e (Å)	D_e (kcal/mole)
Present work		
Minimum Basis	1.420	46.4
Larger Basis	1.352	44.5
Near Hartree-Fock[a]	1.338	50.3
Large Configuration Interaction[b]	1.345	48.8 ± 0.7
Experiment	1.343[c]	56 ± 7[d]

[a]Reference 6.

[b]Reference 8.

[c]R. Horne and R. Colin, Bull Soc. Chim. Belges 81, 93 (1972).

[d]Reference 7.

TABLE II. Chemisorption of hydrogen by clusters of three and four Be atoms. The various clusters are illustrated in the indicated figures. Results in parentheses were obtained using spatially unrestricted SCF wave functions. The absence of parentheses implies that the spatially restricted and unrestricted results were identical.

	r_e (Å)	E (kcal/mole)
Be_3 (3,0)		
Figure 1		
Minimum basis	1.09 (1.25)	4.2 (19.1)
Larger basis	0.93 (1.10)	6.1 (22.0)
Be_4 (3,1)		
Figure 2		
Minimum basis	1.24	28.7
Larger basis	1.17	33.0
Be_4 (4,0)		
Figure 3		
Minimum basis	1.25 (1.26)	65.1 (70.1)
Larger basis	1.17 (1.19)	61.3 (65.4)

TABLE III. Chemisorption on the Be_5 cluster illustrated in Figure 4. Spatially unrestricted calculations gave identical results.

Site	Basis Set	r_e (Å)	E (kcal/mole)
Open	Minimum	1.02	23.2
	Larger	0.91	31.9
Eclipsed	Minimum	1.15	30.1
	Larger	1.06	36.4
Bond Midpoint	Minimum	1.14	32.4
	Larger	1.06	38.1

TABLE IV. Models of the open site for chemisorption of H atoms by beryllium metal. All results reported here were obtained from minimum basis set SCF calculations. When spatially unrestricted results differ, they are indicated in parentheses.

Cluster	Figure	r_e (Å)	E (kcal/mole)
Be_3 (3,0)	1	1.09 (1.25)	4.2 (19.1)
Be_6 (6,0)	5	1.04 (1.18)	38.4 (47.3)
Be_5 (4,1)	4	1.02	23.2
Be_6 (3,3)	6	1.03 (1.11)	37.6 (55.3)
Be_9 (6,3)	7	1.06 (1.13)	33.1 (50.2)

TABLE V. Models of the eclipsed site for chemisorption of H atoms by beryllium metal. The figures cited illustrate the different metal clusters.

Cluster	Figure	r_e (Å)	E (kcal/mole)
Be_4 (3,1)	2	1.24	28.7
Be_5 (4,1)	4	1.15	30.1
Be_7 (6,1)	8	1.11	40.8

TABLE VI. Models of the bond midpoint site.

Cluster	Figure	r_e (Å)	E (kcal/mole)
Be_4 (4,0)	3	1.25 (1.26)	65.1 (70.1)
Be_5 (4,1)	4	1.14	32.4
Be_{10} (10,0)	9	1.15 (1.17)	31.5 (45.3)

TABLE VII. Models of the directly overhead site.

Cluster	Figure	r_e (Å)	E (kcal/mole)
B_e (1,0)	-	1.42	46.4
Be_7 (7,0)	10	1.43	71.3
Be_{10} (7,3)	11	1.42 (1.43)	16.9 (27.3)

TABLE A. Comparison of infinitely separated Be + H with BeH. The first number in each slot comes from a minimum basis calculation, while the second number (in parentheses) arises from the use of the larger basis set. All entries are given in atomic units.

		Be + H		BeH
Total Energy		-14.8757 (-15.0681)		-14.9496 (-15.1391)
Relative Energy		----		- 0.0739 (-0.0710)
r_e		----		2.683 (2.554)
Valence Orbital Energies	$2s_{Be}$	- 0.310 (-0.308)	2σ	- 0.469 (-0.467)
	$1s_H$	- 0.484 (-0.498)	3σ	- 0.321 (-0.307)
Populations				
Be	s	4.00 (4.00)		3.15 (3.06)
	p	0.00 (0.00)		0.81 (0.72)
Total		4.00 (4.00)		3.96 (3.78)
H	s	1.00 (1.00)		1.04 (1.22)
	p	0.00 (0.00)		-- (0.01)
Total		1.00 (1.00)		1.04 (1.23)

TABLE B. Comparison of Be_3 + H with Be_3H. Format is as in Table A.

		Be_3 + H		Be_3H		Spatially Unrestricted
Total Energy		-43.6354 (-44.1935)		-43.6422 (-44.2032)		-43.6658 (-44.2286)
Relative Energy		----		- 0.0068 (- 0.0097)		- 0.0304 (- 0.0254)
r_e		----		2.064 (1.758)		2.363 (2.079)
Valence	$2a_1'$	- 0.473 (-0.474)	$2a_1$	- 0.616 (- 0.638)	4a	- 0.595 (- 0.610)
Orbital	$2e'$	- 0.263 (-0.255)	2e	- 0.270 (-0.259)	5a, 6a	- 0.301, -0.271 (-0.290, -0.263)
Energies	$1s_H$	- 4.484 (-0.498)	$3a_1$	- 0.341 (-0.326)	7a	- 0.322 (- 0.325)
Populations						
Be	s	3.39 (3.60)		3.23 (3.43)		3.41,3.24,2.93 (3.59,2.94,3.59)
	p	0.61 (0.40)		0.80 (0.52)		0.64,0.76,1.00 (0.41,0.75,0.41)
Total		4.00 (4.00)		4.02 (3.95)		4.05,4.00,3.93 (4.00,3.68,4.00)
H	s	1.00 (1.00)		0.93 (1.14)		1.02 (1.31)
	p	0.00 (0.00)		-- (0.01)		-- (0.01)
Total		1.00 (1.00)		0.93 (1.16)		1.02 (1.32)

TABLE C. Comparison of $Be_4(3,1)$ + H with Be_4H. Note, in reference 16, that this Be_4 cluster is nearly, but not precisely, tetrahedral.

		Be_4 + H		Be_4H
Total Energy		-58.0773 (-58.8102)		-58.1229 (-58.8629)
Relative Energy		----		- 0.0456 (-0.0527)
r_e		----		2.352 (2.211)
Valence Orbital Energies	$3a_1$	- 0.544 (-0.535)	$3a_1$	- 0.629 (-0.620)
	2e	- 0.283 (-0.271)	$4a_1$	- 0.406 (-0.395)
	$4a_1$	- 0.277 (-0.265)	2e	- 0.296 (-0.281)
	$1s_H$	- 0.484 (-0.498)	$5a_1$	- 0.251 (-0.239)
Populations				
3 Be	s	3.16 (3.41)		3.11 (3.32)
	p	0.83 (0.58)		0.86 (0.58)
Total		3.99 (3.99)		3.97 (3.91)
1 Be	s	3.15 (3.40)		2.92 (3.07)
	p	0.88 (0.62)		1.15 (0.94)
Total		4.03 (4.02)		4.08 (4.01)
H	s	1.00 (1.00)		1.01 (1.26)
	p	0.00 (0.00)		---- (0.01)
Total		1.00 (1.00)		1.01 (1.27)

TABLE D. Comparison of $Be_4(4,0)$ + H with Be_4H. The two equivalent Be atoms closest to each other are called the near Be atoms.

		Be_4 + H		Be_4H		Spatially Unrestricted	
Total Energy		-57.9890	(-58.7367)	-58.0928	(-58.8345)	-58.1006	(-58.8410)
Relative Energy		----		- 0.1038	(- 0.0978)	- 0.1116	(- 0.1043)
r_e		----		2.354	(2.212)	2.390	(2.249)
Valence	$3a_g$	- 0.525	(-0.527)	$3a_1$ - 0.611	(-0.602)	5a - 0.609	(-0.598)
Orbital	$2b_{2u}$	- 0.371	(-0.366)	$2b_1$ - 0.371	(-0.357)	6a - 0.368	(-0.353)
Energies	$2b_{3u}$	- 0.281	(-0.275)	$4a_1$ - 0.331	(-0.320)	7a - 0.331	(-0.318)
	$4a_g$	- 0.208	(-0.196)	$2b_2$ - 0.273	(-0.258)	8a - 0.275	(-0.259)
				$5a_1$ - 0.242	(-0.224)	9a - 0.281	(-0.263)
Populations							
Near Be	s	3.17	(3.32)	3.13	(3.33)	3.12	(3.28)
	p	0.79	(0.58)	0.95	(0.52)	0.95	(0.67)
Total		3.96	(3.90)	4.08	(3.83)	4.07	(3.95)
Far Be	s	3.47	(3.70)	3.32	(3.51)	3.28, 3.15	(3.41, 3.22)
	p	0.57	(0.40)	0.61	(0.46)	0.59, 0.85	(0.46, 0.73)
Total		4.04	(4.10)	3.93	(3.97)	3.88, 4.00	(3.87, 3.96)
H	s	1.00	(1.00)	0.99	(1.15)	0.99	(1.27)
	p	0.00	(0.00)	----	(0.00_2)	----	(0.01)
Total		1.00	(1.00)	0.99	(1.15)	0.99	(1.28)

TABLE E. Comparison of Be_5 + H with three forms of Be_5H. The "Near Be" atom is the nonequivalent surface atom closer to the atom in second layer, and the "Below Be" atom is just the atom in the second layer (see Figure 4).

		Be_5 + H		Open Be_5H	Eclipsed Be_5H	Bond Midpoint Be_5H
Total Energy		-72.4451 (-73.3627)		-72.4821 (-73.4136)	-72.4931 (-73.4207)	-72.4967 (-73.4234)
Relative Energy		----		- 0.0370 (-0.0509)	- 0.0480 (-0.0580)	- 0.0516 (-0.0607)
r_e		----		1.934 (1.718)	2.180 (2.009)	2.145 (2.006)
Valence	5a'	- 0.579 (-0.572)	5a'	- 0.681 (-0.679)	- 0.668 (-0.660)	- 0.673 (-0.661)
Orbital	6a'	- 0.390 (-0.383)	6a'	- 0.491 (-0.484)	- 0.440 (-0.431)	- 0.446 (-0.435)
Energies	2a''	- 0.294 (-0.285)	7a'	- 0.348 (-0.331)	- 0.403 (-0.389)	- 0.392 (-0.379)
	7a'	- 0.292 (-0.281)	2a''	- 0.310 (-0.298)	- 0.308 (-0.295)	- 0.309 (-0.295)
	8a'	- 0.223 (-0.210)	8a'	- 0.236 (-0.224)	- 0.240 (-0.225)	- 0.247 (-0.233)
	$1s_H$	- 0.484 (-0.498)	9a'	- 0.296 (-0.285)	- 0.263 (-0.251)	- 0.275 (-0.264)
Populations						
2 Be	s	3.04 (3.25)		2.99 (3.14)	3.04 (3.21)	3.02 (3.19)
	p	0.98 (0.74)		1.01 (0.73)	0.97 (0.72)	1.04 (0.76)
Total		4.02 (3.99)		4.00 (3.87)	4.01 (3.93)	4.06 (3.95)
Near Be	s	3.21 (3.47)		3.34 (3.52)	3.27 (3.53)	3.41 (3.63)
	p	0.82 (0.57)		0.64 (0.46)	0.78 (0.52)	0.56 (0.38)
Total		4.03 (4.04)		3.98 (3.98)	4.06 (4.04)	3.97 (4.01)
Far Be	s	3.49 (3.64)		3.50 (3.69)	3.46 (3.53)	3.54 (3.63)
	p	0.48 (0.36)		0.55 (0.36)	0.44 (0.34)	0.38 (0.29)
Total		3.97 (3.99)		4.05 (4.05)	3.89 (3.86)	3.92 (3.93)
Below Be	s	3.08 (3.38)		2.91 (3.07)	2.92 (3.06)	2.94 (3.06)
	p	0.86 (0.61)		1.01 (0.82)	1.09 (0.90)	1.04 (0.86)
Total		3.95 (3.99)		3.92 (3.90)	4.01 (3.96)	3.98 (3.92)
H	s	1.00 (1.00)		1.06 (1.32)	1.02 (1.27)	1.01 (1.24)
	p	0.00 (0.00)		---- (0.01)	---- (0.01)	---- (0.01)
Total		1.00 (1.00)		1.06 (1.33)	1.02 (1.28)	1.01 (1.25)

TABLE F. Comparison of Be_6 + H with Be_6H for two different Be_6 clusters. All calculations employed a minimum basis set.

		$Be_6(3,3)$ + H		Be_6H		Spatially Unrestricted
Total Energy		-86.8524		-86.9124		-86.9405
Relative Energy		----		- 0.0600		- 0.0881
r_e		----		1.947		2.107
Valence Orbital Energies	$2a_g$	- 0.585	$3a_1$	- 0.644	7a	- 0.642
	$2e_u$	- 0.360	$4a_1$	- 0.479	8a	- 0.481
	$2a_u$	- 0.338	3e	- 0.363	9a, 10a	- 0.364, -0.361
	$2e_g$	- 0.207	4e	- 0.210	11a, 12a	- 0.248, -0.210
	$1s_H$	- 0.484	$5a_1$	- 0.294	13a	- 0.229
Populations						
Above 3 Be	s	2.78		2.64		2.78, 2.78, 2.74
	p	1.22		1.37		1.24, 1.24, 1.31
Total		4.00		4.01		4.02, 4.02, 4.05
Below 3 Be	s	2.78		2.70		2.73, 2.65, 2.74
	p	1.22		1.28		1.22, 1.31, 1.22
Total		4.00		3.98		3.96, 3.95, 3.96
H	s	1.00		1.01		1.05

TABLE F. Continued

		$Be_6(6,0) + H$		Be_6H		Spatially Unrestricted
Total Energy		-86.8205		-86.8817		-86.8958
Relative Energy		----		- 0.0612		- 0.0753
r_e		----		1.958		2.224
Valence Orbital Energies		$3a_1'$ - 0.527		$3a_1$ - 0.639	7a	- 0.612
		$3e'$ - 0.407		3e - 0.411	8a, 9a	- 0.410, -0.404
		$4a_1'$ - 0.264		$4a_1$ - 0.357	10a	- 0.353
		$4e'$ - 0.224		4e - 0.222	11a, 12a	- 0.239, -0.220
		$1s_H$ - 0.484		$5a_1$ - 0.276	13a	- 0.272
Populations						
Inner 3 Be	s	2.92		2.89		2.69, 2.69, 2.92
	p	1.14		1.23		1.39, 1.39, 1.26
Total		4.07		4.12		4.07, 4.08, 4.18
Outer 3 Be	s	3.24		3.15		3.24, 3.26, 3.24
	p	0.69		0.72		0.63, 0.66, 0.63
Total		3.93		3.87		3.87, 3.92, 3.87
H	s	1.00		1.03		1.00

TABLE G. Comparison of $Be_7(6,1)$ + H with Be_7H.

		$Be_7(6,1)$ + H		Be_7H
Total Energy		-101.2435		-101.3085
Relative Energy		----		- 0.0650
r_e		----		2.099
Valence Orbital Energies	$4a_1$	- 0.590		- 0.666
	3e	- 0.415		- 0.428
	$5a_1$	- 0.309		- 0.419
	$6a_1$	- 0.263		- 0.305
	4e	- 0.223		- 0.230
	$1s_H$	- 0.484	$(7a_1)$	- 0.270
Populations				
Inner 3 Be	s	2.93		2.94
	p	1.26		1.27
Total		4.19		4.21
Outer 3 Be	s	3.27		3.19
	p	0.61		0.63
Total		3.88		3.82
Below Be	s	3.22		2.99
	p	0.58		0.90
Total		3.79		3.89
H	s	1.00		1.02

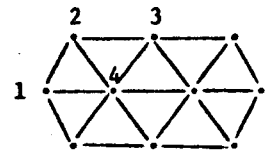
TABLE H. Comparison of $Be_7(7,0)$ + H with Be_7H.

		$Be_7(7,0)$ + H		Be_7H
Total Energy		-101.2675		-101.3813
Relative Energy		----		- 0.1138
r_e		----		2.694
Valence Orbital Energies	$3a_{1g}$	- 0.554	$3a_1$	- 0.584
	$2e_{1u}$	- 0.447	$2e_1$	- 0.431
	$2e_{2g}$	- 0.302	$2e_2$	- 0.297
	$1b_{2u}$	- 0.235	$1b_2$	- 0.234
	$4a_{1g}$	- 0.217	$4a_1$	- 0.371
	$1s_H$	- 0.484	$5a_1$	- 0.234
Populations				
Six Equivalent Be	s	2.97		2.94
	p	1.04		1.01
Total		4.01		3.95
Unique Be	s	2.97		2.67
	p	0.97		1.67
Total		3.94		4.35
H	s	1.00		0.93

TABLE I. Comparison of $Be_9(6,3)$ + H with Be_9H.

		$Be_9(6,3)$ + H		Be_9H		Spatially Unrestricted
Total Energy		-130.0614		-130.1142		-130.1414
Relative Energy		----		- 0.0528		0.0800
r_e		----		2.003		2.144
Valence	$4a_1$	- 0.663		- 0.703	10a	- 0.697
Orbital	4e	- 0.488		- 0.493	11a, 12a	- 0.501, -0.498
Energies	$5a_1$	- 0.399		- 0.506	13a	- 0.494
	$6a_1$	- 0.298		- 0.337	14a	- 0.344
	5e	- 0.282		- 0.280	15a, 16a	- 0.281, -0.280
	6e	- 0.212		- 0.211	17a, 18a	- 0.245, -0.215
	$1s_H$	- 0.484	($7a_1$)	- 0.288	19a	- 0.268
Populations						
Inner 3 Be	s	2.90		2.85		2.79, 2.72, 2.79
	p	1.11		1.26		1.32, 1.32, 1.32
Total		4.00		4.10		4.12, 4.04, 4.12
Outer 3 Be	s	2.92		2.99		3.09, 3.09, 3.00
	p	1.00		0.89		0.83, 0.83, 0.92
Total		3.92		3.88		3.92, 3.92, 3.92
Below 3 Be	s	3.00		2.93		2.88, 2.88, 2.73
	p	1.07		1.13		1.14, 1.14, 1.25
Total		4.08		4.05		4.02, 4.02, 3.98
H	s	1.00		0.89		0.94

TABLE J. Comparison of $Be_{10}(10,0)$ + H with $Be_{10}H$. Atoms are labelled according to



	Be_{10} (10,0) + H	$Be_{10}H$	Spatially Unrestricted
Total Energy	-144.5449	-144.5951	-144.6172
Relative Energy	----	- 0.0502	- 0.0723
r_e	----	2.182	2.203
Valence	$5a_g$ - 0.545	$5a_1$ - 0.626	11a - 0.627
Orbital	$4b_{3u}$ - 0.490	$4b_1$ - 0.493	12a - 0.500
Energies	$3b_{2u}$ - 0.439	$3b_2$ - 0.456	13a - 0.458
	$6a_g$ - 0.401	$6a_1$ - 0.454	14a - 0.453
	$2b_{1g}$ - 0.386	$2a_2$ - 0.393	15a - 0.394
	$5b_{3u}$ - 0.284	$5b_1$ - 0.293	16a - 0.340
	$4b_{2u}$ - 0.278	$4b_2$ - 0.275	17a - 0.293
	$7a_g$ - 0.249	$7a_1$ - 0.339	18a - 0.283
	$3b_{1g}$ - 0.240	$3a_2$ - 0.240	19a - 0.248
	$1b_{1u}$ - 0.211	$8a_1$ - 0.249	20a - 0.233
	$1s_H$ - 0.484	$9a_1$ - 0.176	21a - 0.227
Populations			
End 2 Be (#1) s	2.93	2.92	2.91,2.94
p	1.09	1.07	1.08,1.05
Total	4.01	4.00	3.98,3.98
4 Equivalent Be (#2) s	2.89	2.87	2.96,2.87,2.89,2.87
p	1.09	1.08	1.02,1.14,1.05,1.06
Total	3.97	3.96	3.98,4.01,3.94,3.94
2 Above and Below (#3) s	2.76	2.84	2.80,2.86
p	1.23	1.13	1.17,1.10
Total	3.99	3.98	3.97,3.96
2 Left and Right (#4) s	2.57	2.53	2.56,2.56
p	1.48	1.59	1.54,1.59
Total	4.05	4.12	4.10,4.15
H s	1.00	0.98	0.98

TABLE K. Comparison of $Be_{10}(7,3)$ + H with $Be_{10}H$.

	$Be_{10}(7,3)$ + H		$Be_{10}H$		Spatially Unrestricted	
Total Energy		-144.5456		-144.5725		-144.5890
Relative Energy		----		- 0.0269		- 0.0434
r_e		----		2.695		2.710
Valence	$4a_1$	- 0.673	$4a_1$	- 0.678	11a	- 0.681
Orbital	4e	- 0.518	4e	- 0.519	12a,13a	- 0.522, -0.519
Energies	5a	- 0.409	$5a_1$	- 0.491	14a	- 0.492
	5e	- 0.331	5e	- 0.336	15a,16a	- 0.346, -0.341
	$6a_1$	- 0.290	$6a_1$	- 0.329	17a	- 0.332
	$7a_1$	- 0.240	$7a_1$	- 0.243	18a	- 0.259
	6e	- 0.239	6e	- 0.232	19a,20a	- 0.248, -0.231
	$8a_1$	- 0.484	$8a_1$	- 0.288	21a	- 0.258

Populations

6 Be	s	2.88	2.89	2.92,2.87,2.89,2.89,2.87,2.93
	p	1.09	1.05	1.03,1.06,1.05,1.05,1.06,1.03
Total		3.97	3.94	3.95,3.93,3.94,3.94,3.93,3.95
3 Be	s	2.93	2.90	2.95,2.84,2.96
	p	1.13	1.15	1.07,1.15,1.07
Total		4.05	4.05	4.02,3.99,4.03
1 Be	s	2.74	2.71	2.73
	p	1.26	1.68	1.69
Total		4.00	4.39	4.41
H	s	1.00	0.86	0.89

Figure Captions

Figure 1. Three Be atom model for the open site for chemisorption.

Figure 2. Four Be atom model for the eclipsed site for chemisorption.

Figure 3. Four Be atom model for the bond midpoint site for chemisorption.

Figure 4. Five Be atom model for the open, eclipsed, and bond midpoint sites for chemisorption.

Figure 5. Six Be atom model for the open site for chemisorption.

Figure 6. A second six atom model for the open site for chemisorption.

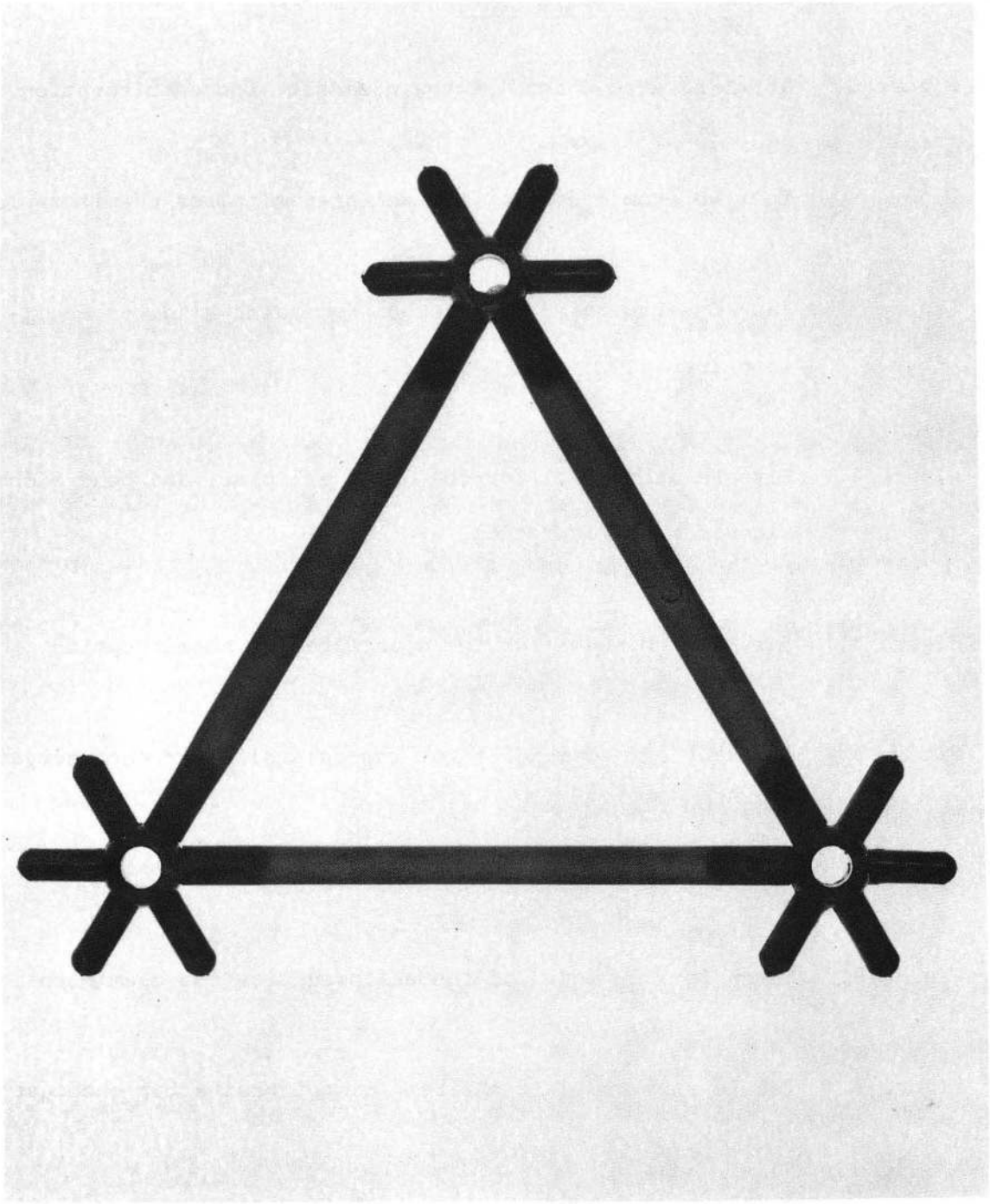
Figure 7. Nine atom model of the open site for chemisorption.

Figure 8. Seven Be atom model of the eclipsed site for chemisorption.

Figure 9. Ten Be atom model of the bond midpoint site for chemisorption.

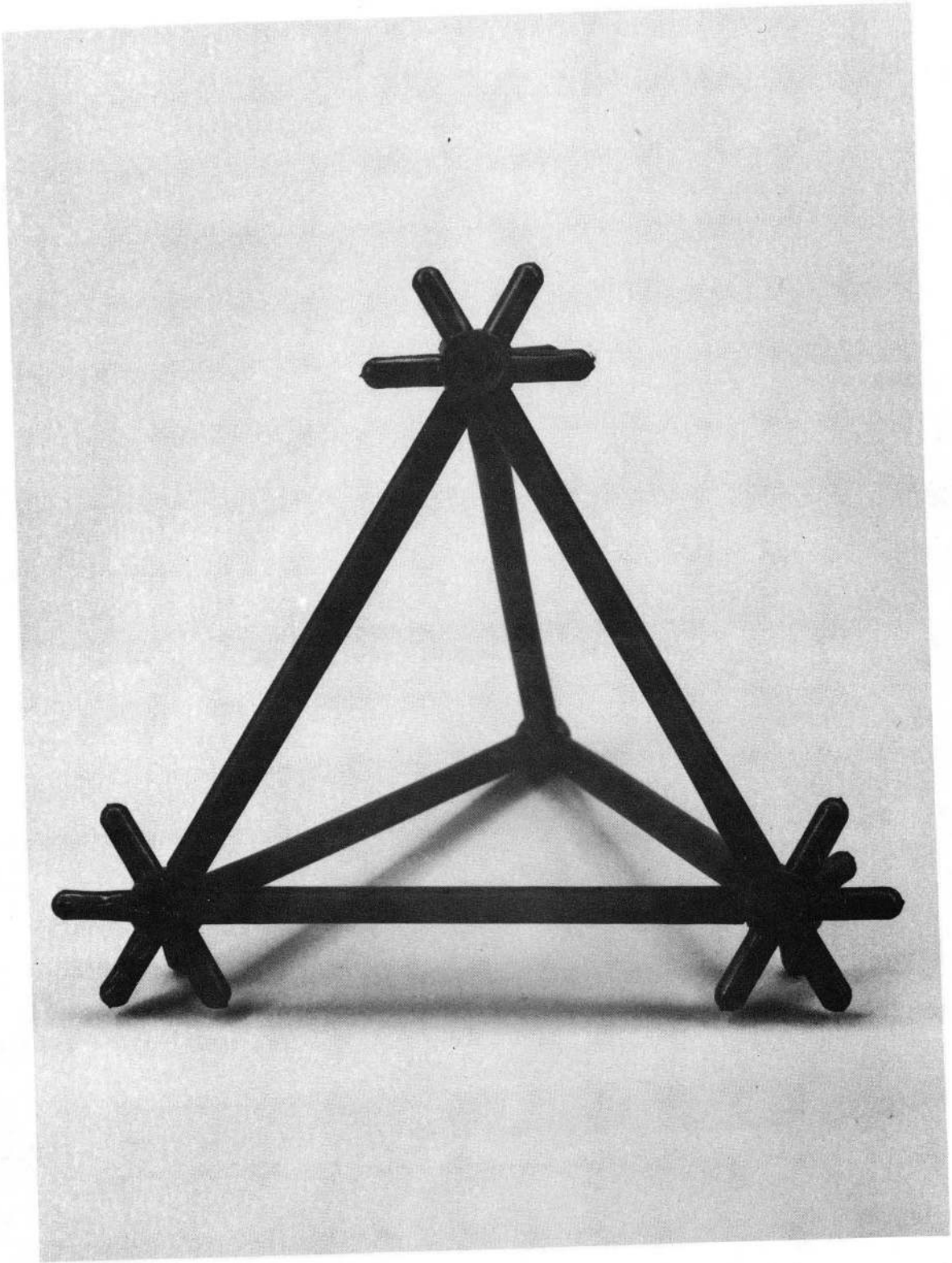
Figure 10. Seven Be atom model of the directly overhead site for chemisorption.

Figure 11. Ten Be atom model of the directly overhead site for chemisorption.



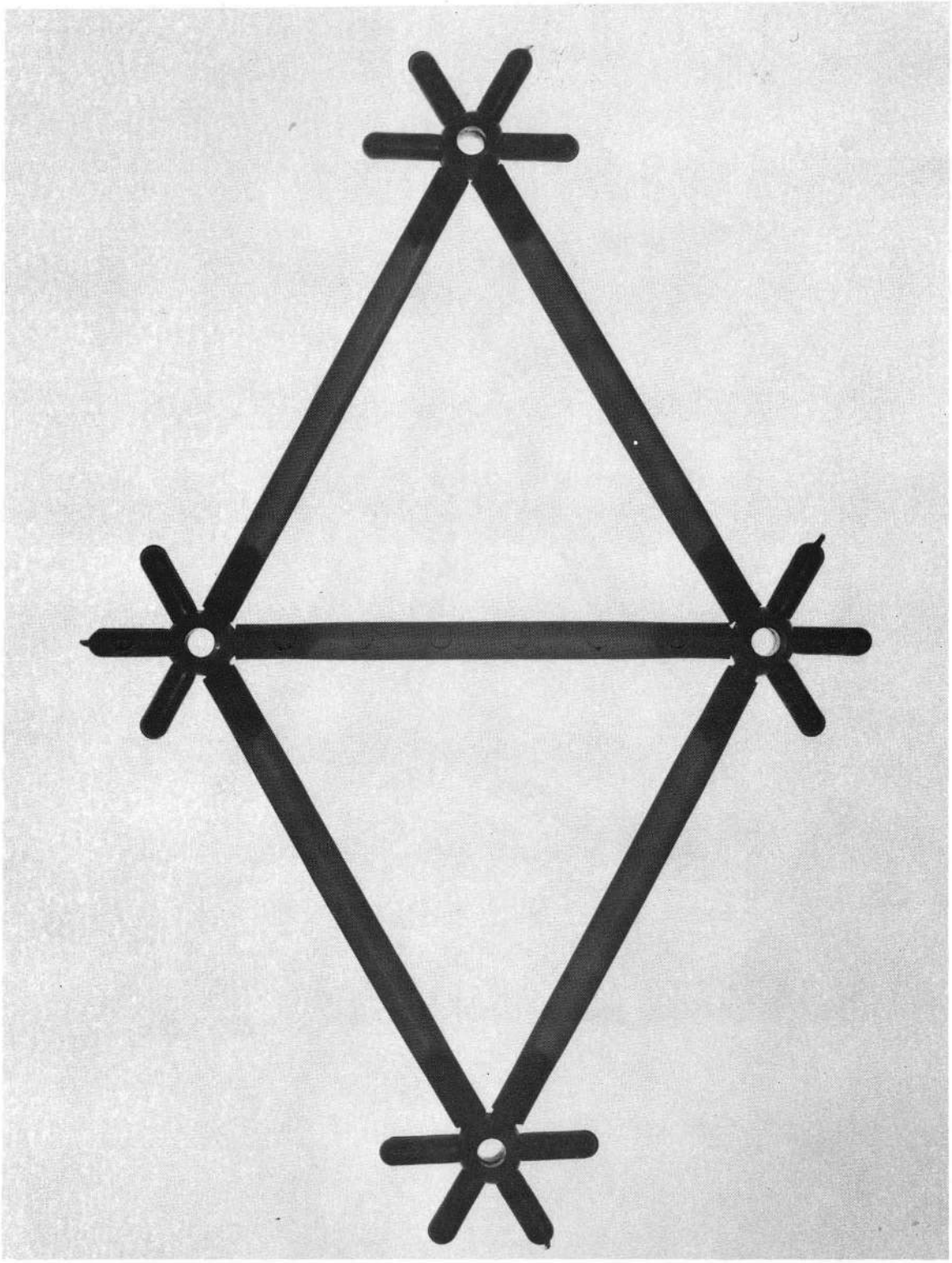
XBB 746-3870

Fig. 1



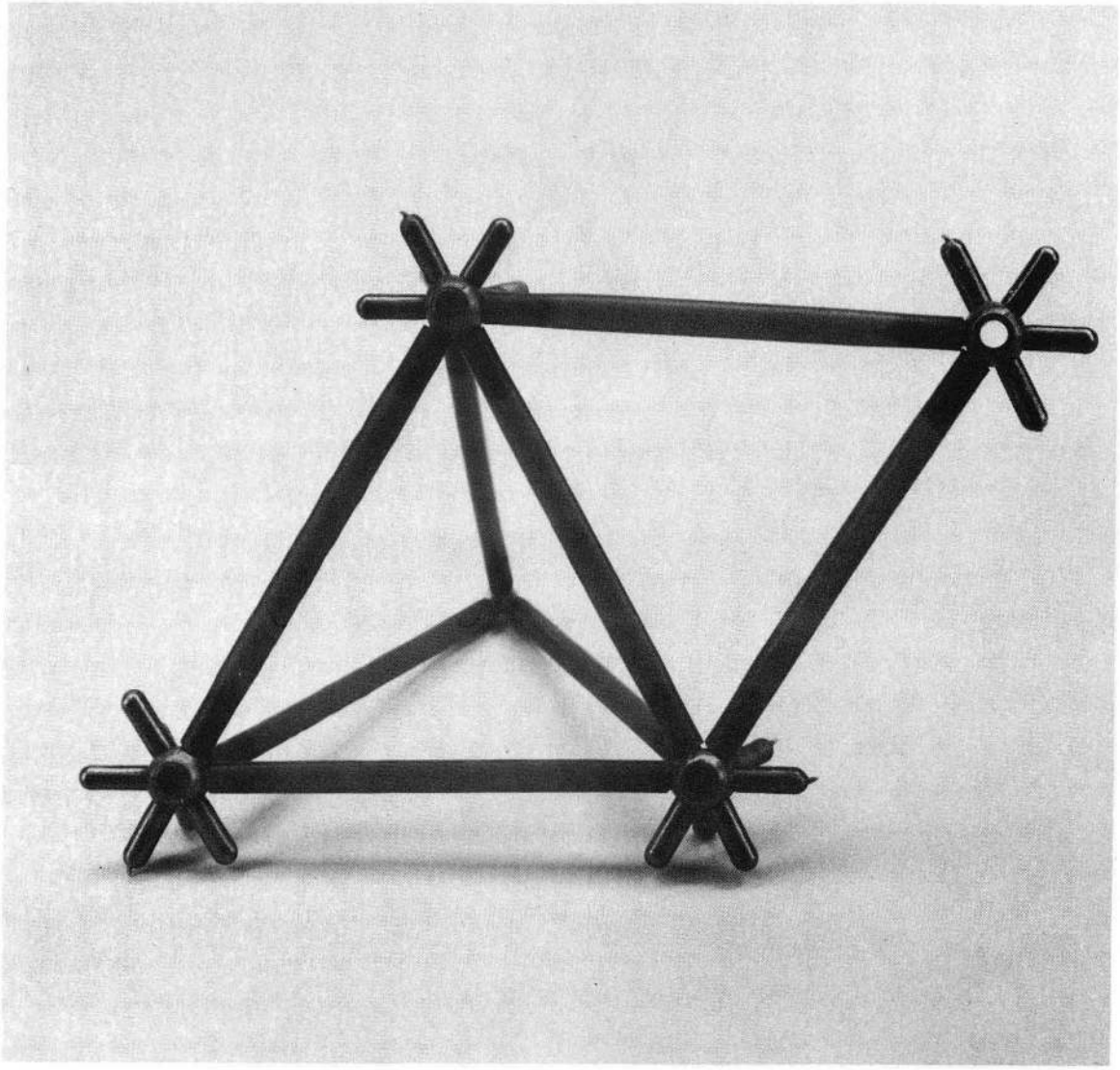
XBB 746-3875

Fig. 2



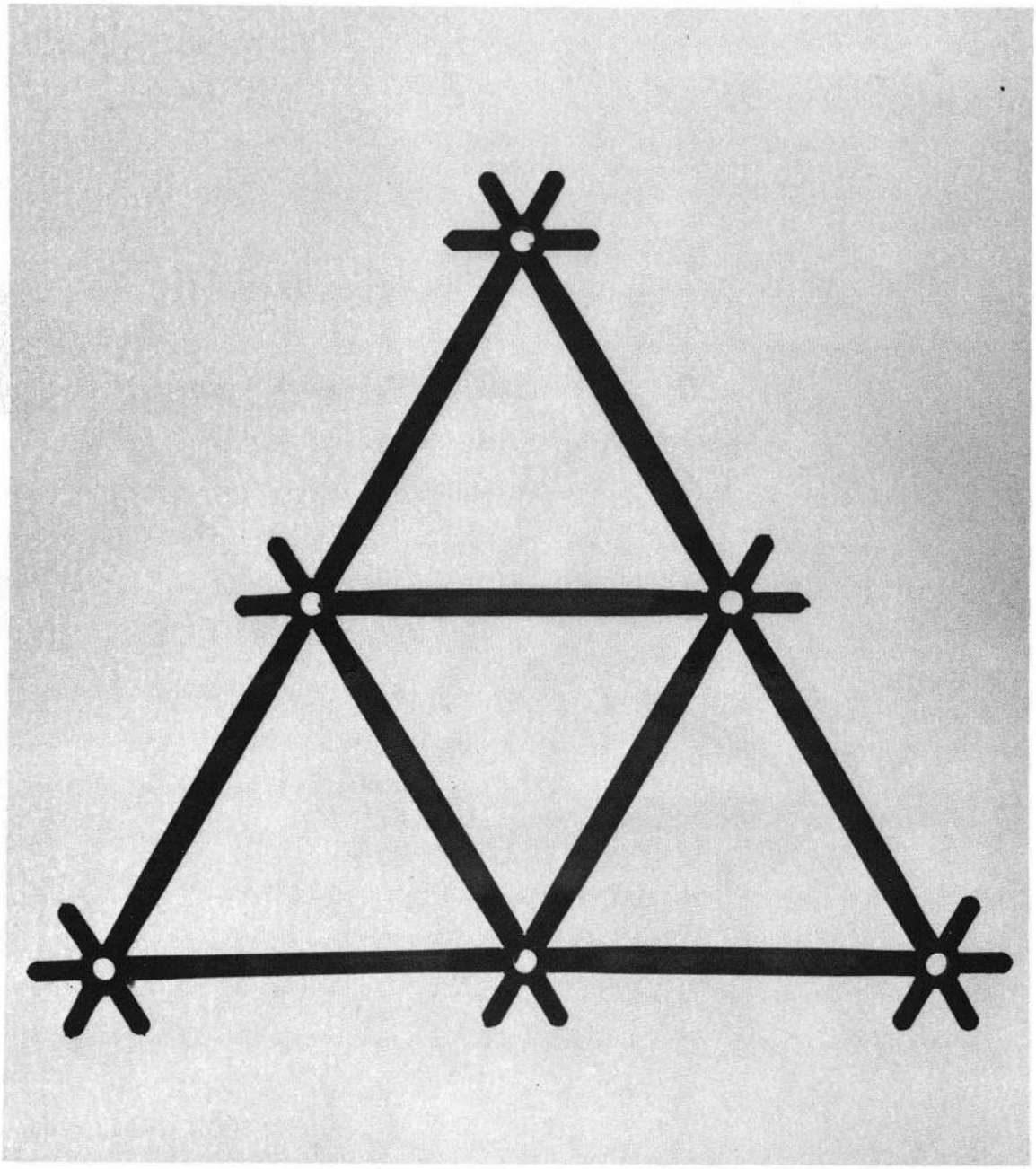
XBB 746-3871

Fig. 3



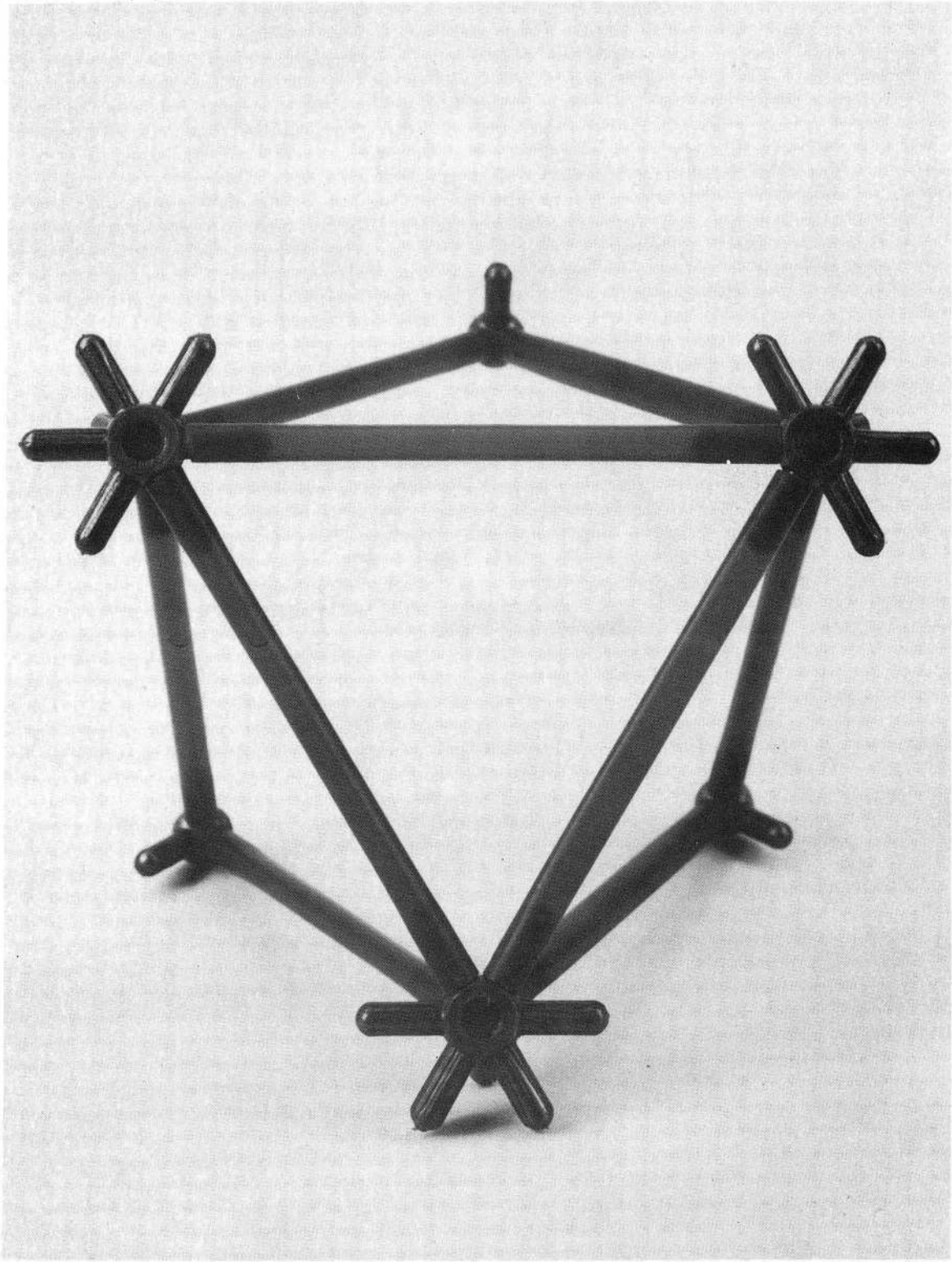
XBB 746-3879

Fig. 4



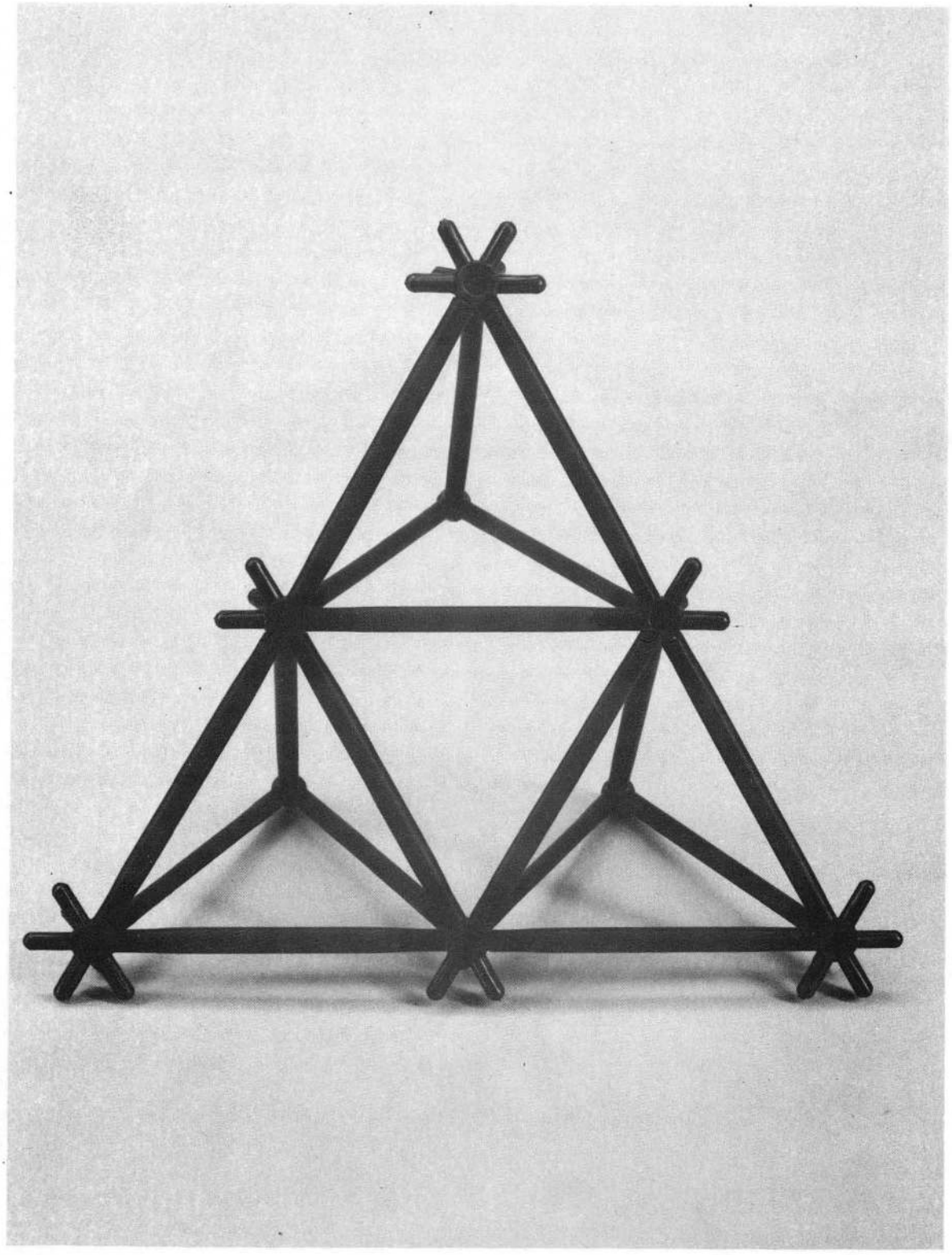
XBB 746-3872

Fig. 5



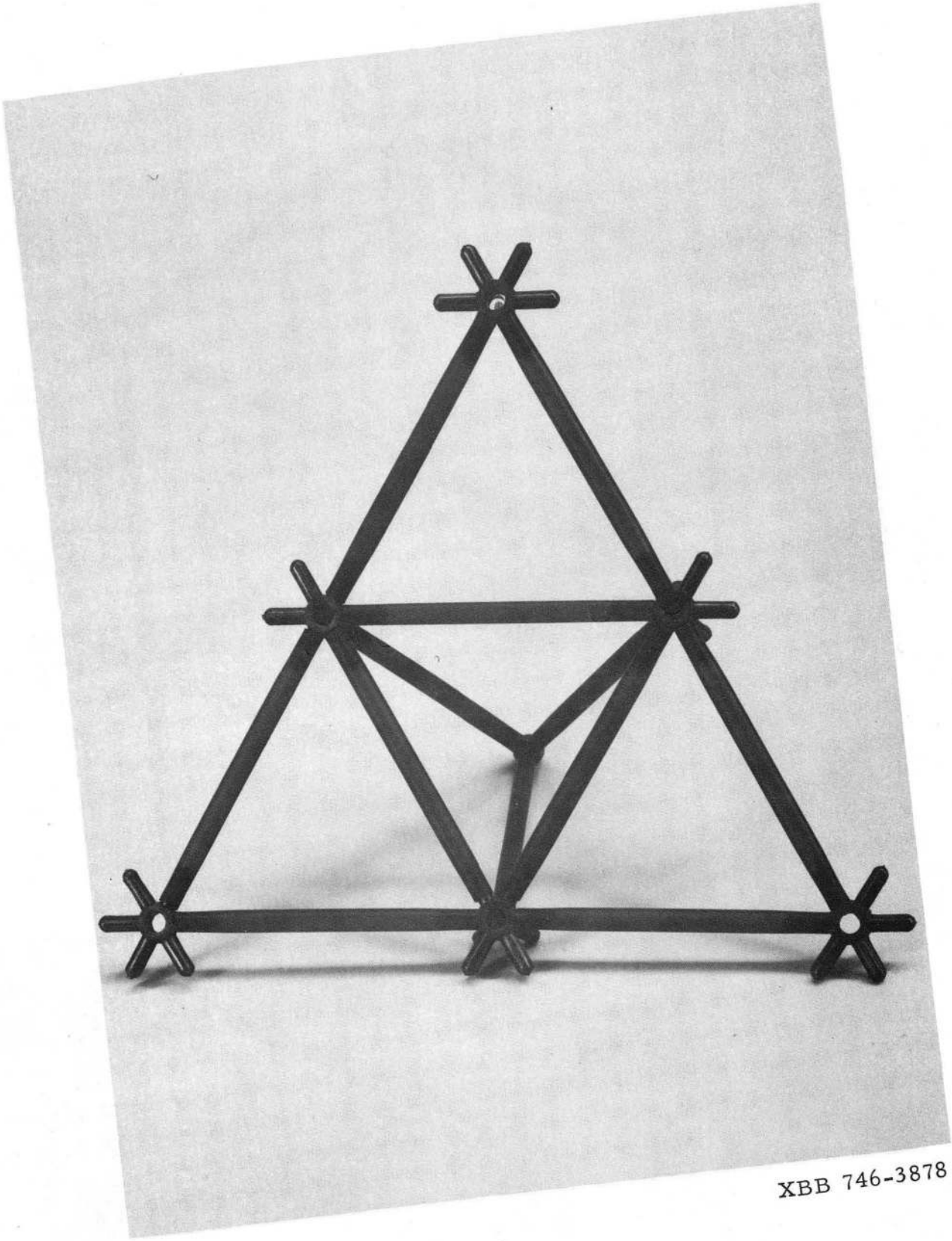
XBB 746-3876

Fig. 6



XBB 746-3880

Fig. 7



XBB 746-3878

Fig. 8

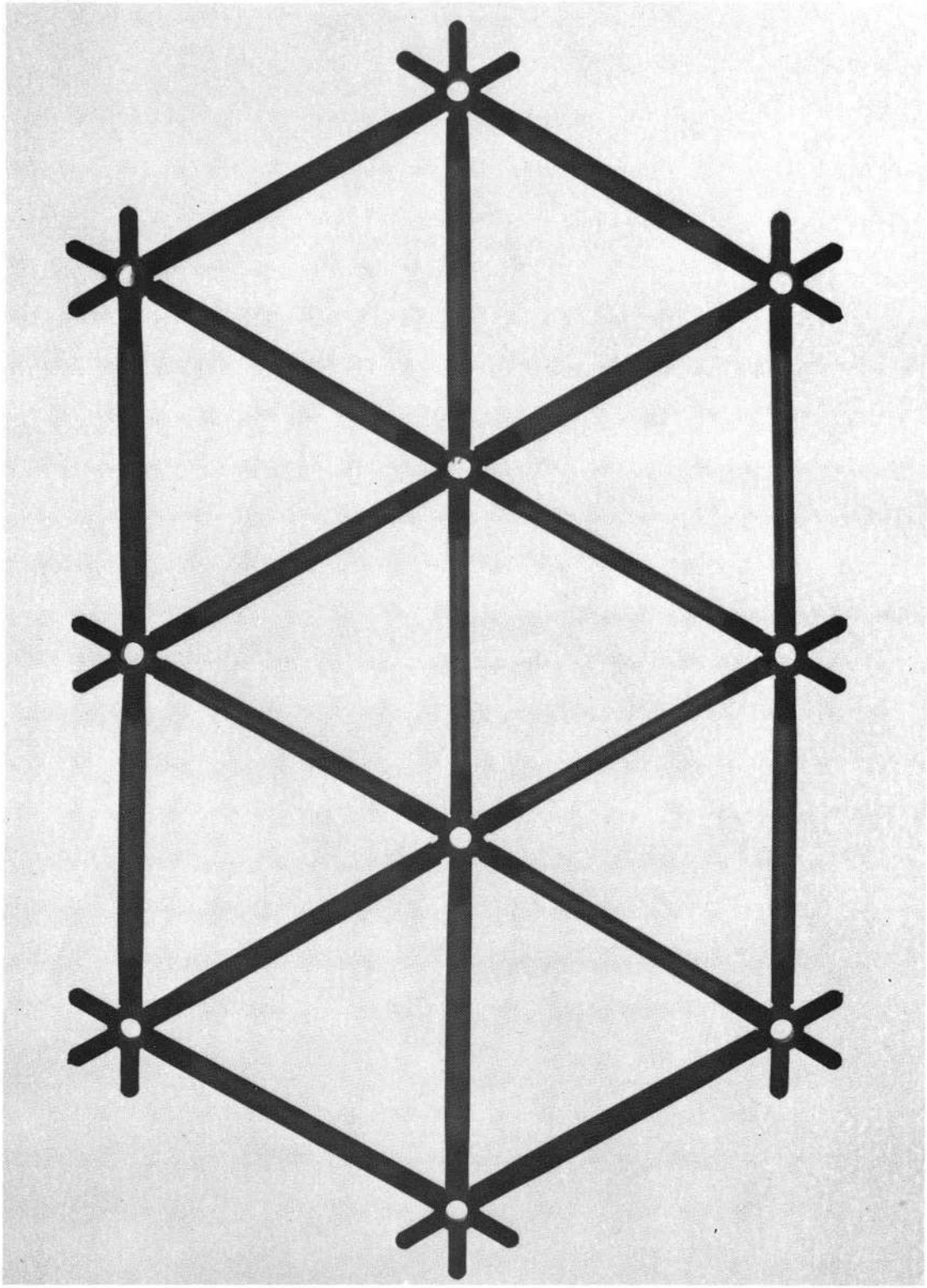
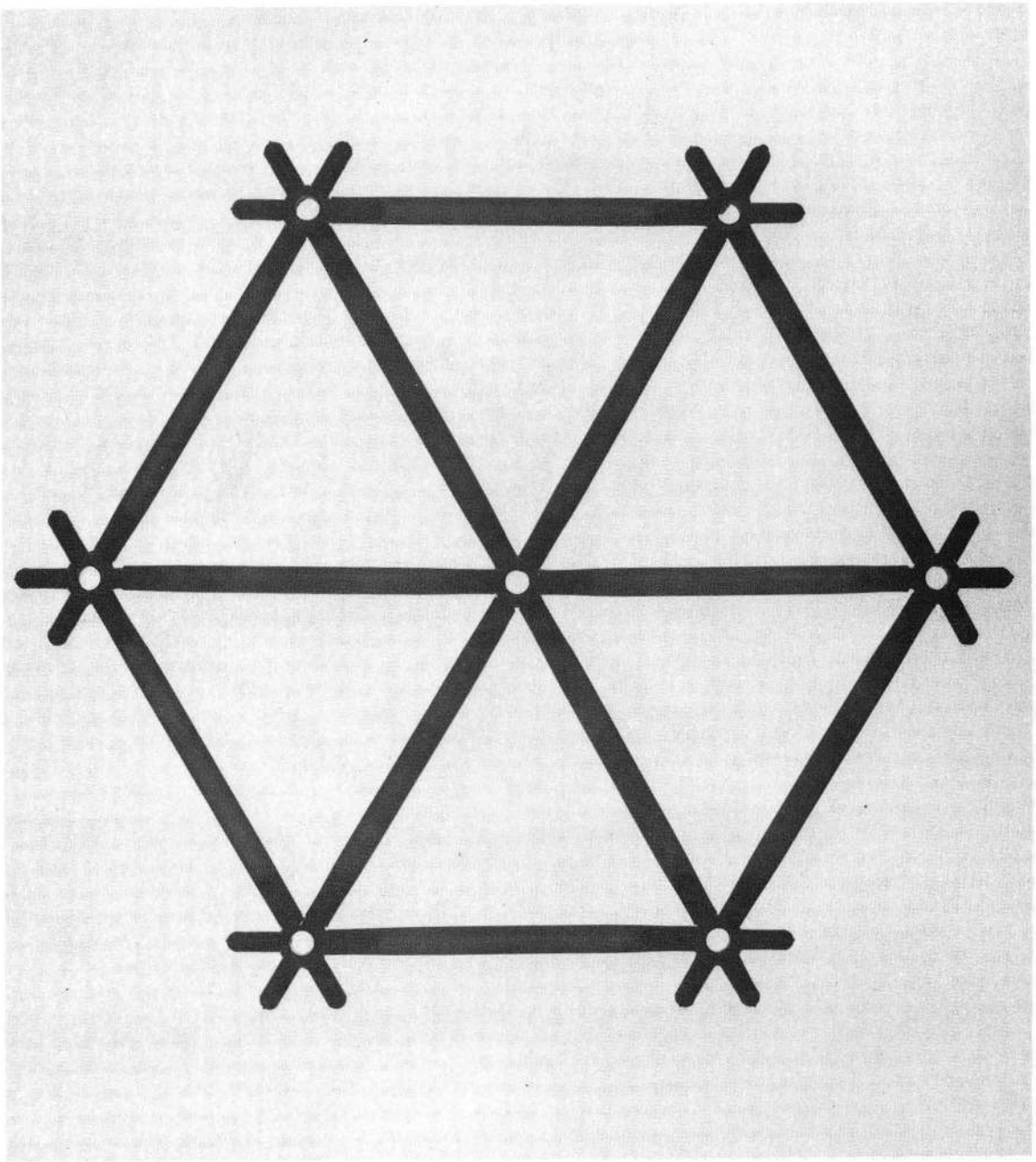
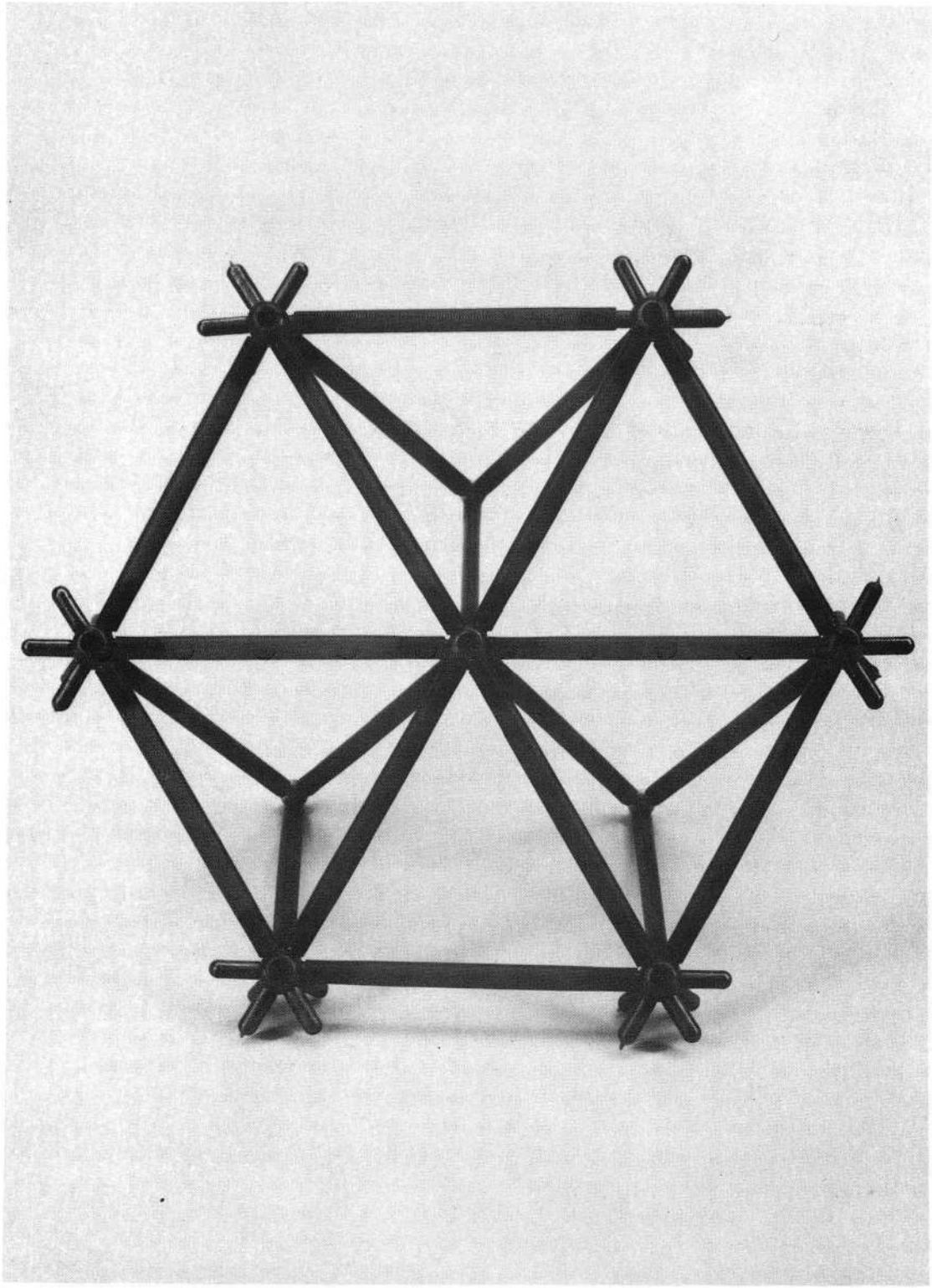


Fig. 9



XBB 746-3873

Fig. 10



XBB 746-3877

Fig. 11

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