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ADSORBED ON SINGLE CRYSTAL METAL SURFACES

A. Gavezzotti, M. Simonetta, M.A. Van Hove,
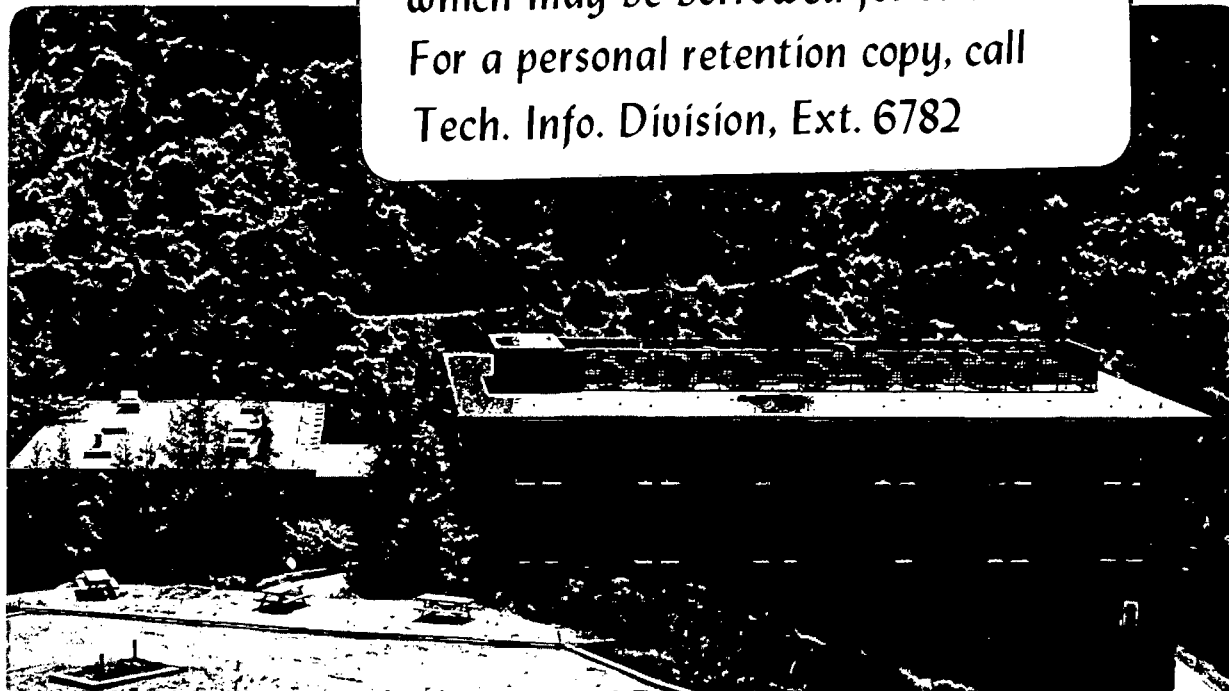and G.A. Somorjai

June 1982

DISCLAIMER

FORCE-FIELD CALCULATIONS OF THE PACKING ENERGY OF MONOLAYERS

OF C_3 AND C_4 HYDROCARBON MOLECULES ADSORBED ON SINGLE CRYSTAL METAL SURFACES

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ABSTRACT

Force-field calculations are applied to investigate the packing energy of overlayers of C_3 and C_4 hydrocarbons adsorbed on Pt(111) and Rh(111), in which Van der Waals adsorbate-adsorbate interactions play a significant role. The packing energies are used to compare various adsorbate structures for which Low Energy Electron Diffraction patterns have been obtained and corresponding detailed structures have been proposed. In particular, the conformation of methylacetylene ($HCCCH_3$) in a (2x2) arrangement, and of propylidyne ($\equiv CCH_2CH_3$) and butylidyne ($\equiv CCH_2CH_2CH_3$) in (2x2), c(4x2) and ($2\sqrt{3}x2\sqrt{3}$)R30° arrangements are considered.

1. INTRODUCTION AND METHOD OF CALCULATION

During the study of the structure of adsorbed monolayers on clean metal sur-
faces, one is often faced with the problem of determining the best packing arrange-
ment of the adsorbate molecules. When adsorbate-adsorbate forces can be decoupled
from adsorbate-surface bonding, the problem is the two-dimensional equivalent of
the packing structure analysis which is often carried out with success on three-
dimensional molecular organic crystals. The use of van der Waals-type potentials
gives results of high accuracy in the calculations of such crystal properties as
sublimation energies, rotational barriers, lattice vibrations and crystal free
energies,[1a,b] as well as in the calculation of optimum geometries for isolated
molecules.[1c]

A monolayer of adsorbed organic molecules or radicals is regarded as a two-
dimensional slice of an organic crystal; the dimensions of the unit cell can be
readily derived from analysis of LEED patterns, while complete space-group sym-
metry and the detailed structural analysis of the asymmetric unit require,
for example, calculation of I-V curves for low energy electron diffraction (LEED)
spots. One has to make LEED I-V calculations for all plausible surface structures
and pick out the one structure that produces the best fit with the experimental
I-V curves. Since this step is computationally quite involved, however, it is
important to have preliminary information regarding steric hindrance, that might
at once rule out some impossible, overcrowded structures.

Steric hindrance appears to play an important role in monolayers of hydro-
carbon molecules adsorbed on single-crystal metal surfaces. Here the lattice of
the substrate surface often imposes certain adsorption sites that may not be ideal
from the point of view of molecular packing. This leaves some freedom of move-
ment for the molecular parts most distant from the substrate. Such is the case in

alkylidyne adsorbates, $\equiv C(CH_2)_n CH_3$, such as for propylidyne (CCH_2CH_3) and butylidyne ($\equiv CCH_2CH_2CH_3$) adsorbed on Rh(111) and Pt(111) and for other adsorption systems to be described in the next section. In these an ethyl or propyl group is free to rotate about certain C-C bond axes to the extent allowed by steric hindrance of the neighboring molecules.

The procedure we have followed to gauge structural stability on non-bonded interaction grounds has been outlined in previous papers.[2] Basically, the non-bonded Van der Waals packing potential energy (PPE) of a molecule in a monolayer is evaluated as

$$E = \sum_{i,j} A \exp(-BR_{ij}) - CR_{ij}^{-6}$$

where i runs over the atoms of the molecule, and j runs over the atoms of a number of symmetry-generated neighboring molecules. A, B and C are parameters to be determined for each type of interatomic contact.[3] In this way, a) the relative energies of different overlayer structures can be evaluated and b) the effects of displacing a molecule from its equilibrium position in the field of the surrounding ones can be calculated. These energy differences have a great influence on the ease of formation and on the ease of ordering of a surface mono-layer of organic molecules. It is important to remind once again that adsorbate-substrate effects are neglected, as it is supposed that they remain largely constant when the molecules are displaced, rotated or distorted at the surface. The cases we shall be interested in satisfy this condition to a large extent.

The computer program used in the calculations (written by one of us, A.G.) is the same used for crystal packing analyses of organic molecules[4] and for studies of molecular motions in organic crystals,[2] with only minor adaptations.

2. EXPERIMENTAL BACKGROUND: C_3 AND C_4 HYDROCARBON STRUCTURES ON Pt(111) AND Rh(111)

We apply the force-field calculations described in the Introduction to some structures adopted by C_3 and C_4 hydrocarbon molecules on the (111) surface of single crystal platinum and rhodium substrates. Those structures have been studied by LEED and other ultra-high vacuum techniques, along with various investigations of C_2 hydrocarbons on the same substrates.[5] The main results to consider here are the following.

With acetylene (C_2H_2) and ethylene (C_2H_4) one can obtain both an intact, though distorted species, that is parallel-bonded to the surface, and a transformed species with a C-C axis perpendicular to the surface, the latter being ethylidyne ($\equiv CCH_3$) bonded to three metal atoms. These molecules can form well-ordered (2 x 2) arrays at a 1/4 monolayer coverage, in which steric hindrance plays a negligible role. On Rh(111) a c(4 x 2) structure can also be formed at the same coverage, whose detailed structure is uncertain: from HREELS data it may be ethylidyne again, but this model (or any other model) does not satisfy a LEED intensity analysis. We show ethylidyne structures in Figure 1.

With methylacetylene (C_3H_4) and propylene (C_3H_6), there is much evidence that adsorption structures similar to those of the C_2's form. For example, methylacetylene in a (2 x 2) array is believed to be parallel-bonded, because its LEED I-V curves are identical to those of (2 x 2) acetylene, which can be explained by simple substitution of methyl groups for hydrogen atoms in the acetylene adsorbate, with random methyl orientation. A possible (2 x 2) structure for methylacetylene is shown in Figure 2. We have chosen to investigate with the force-field calculation approach which forms of randomness in the methyl group orientation are plausible.

Another kind of structure was also chosen for such an investigation. It concerns the analogue of ethylidyne for C_3 and C_4 molecules, namely propylidyne and butylidyne, cf. Figure 3, which also shows some bond lengths as determined

by LEED. With similar observations and arguments we assume that the propylidyne species ($\equiv CCH_2CH_3$) forms, whose structure is obtained from ethylidyne by substitution of methyl groups for hydrogen atoms. At a 1/4 monolayer coverage, the ethyl groups can be randomly oriented or they can order, at least on Rh(111), in a (2 $\sqrt{3}$ x 2 $\sqrt{3}$)R30° array, which, presumably, again occurs because of steric hindrance. A possible arrangement is illustrated in Figure 4, with the three molecules of one unit cell shown in more detail in Figure 5. This structure has p31m symmetry, and if we allow the ethyl groups to rotate in unison about surface normals, a p3 symmetry can be kept. We shall investigate the effect on the PPE of this simultaneous rotation, in which, for example, the three molecules in Figure 5 would rotate simultaneously towards each other. An approximate LEED intensity analysis of this structure favors such a rotation towards closer packing by about 30° about the surface normal.[6]

A c(4 x 2) structure can also be formed for C_3's adsorbed on Rh(111), with LEED I-V curves identical to those of the corresponding C_2 species; again, we believe that substitution of methyl groups for hydrogen atoms can explain the observations, together with disorder in the ethyl group orientations.

With adsorption of cis-2-butene or trans-2-butene on Pt(111), one can produce species that, with similar arguments as for propylidyne, are believed to be butylidyne, cf. Figure 3. At a 1/4 monolayer coverage, one can have randomness in the orientation of the propyl ($-CH_2CH_2CH_3$) groups and also ordering into a (2 $\sqrt{3}$ x 2 $\sqrt{3}$)R30° array, similar to the ordering for propylidyne on Rh(111). The transformations between the various structures described here occur at different temperatures and sometimes require the presence of extra hydrogen. Where needed in the forthcoming discussions, we shall point out these details.

3. RESULTS OF FORCE-FIELD CALCULATIONS

The upright propylidyne species is, in many ways, the first choice for the application of the monolayer packing energy method. First, hydrocarbon Van der Waals potentials are the best known in organic crystallography;[3a] and second, the torsional motions around the C-CH$_2$ and H$_2$C-CH$_3$ bonds are not likely to disturb the C-surface bond, whose energy should remain constant. Therefore, it was decided to calculate the packing potential energy for the p(2 x 2), c(4 x 2) and (2√3 x 2√3)R30° structures for propylidyne on Rh(111) and Pt(111), thereby making the uncertain assumption that the c(4 x 2) species is really propylidyne.

Figure 6 shows the PPE curves for simultaneous rotation of all mlecules in the monolayer around the C-CH$_2$ axis, preserving in each case the space group symmetry. Analogous curves for the rotation of only one molecule in a fixed environment show essentially the same features, and are shown in Figure 7. Both p(2x2) and c(4x2) can be described as p1 cells, while the (2 √3 x 2 √3)R30° structure belongs to space group p31m for θ = 0, and p3 for θ ≠ 0. There is no clear preference among the three structures, whose PPE's are almost the same on each metal. The PPE on Rh(111) is calculated to be slightly larger than on Pt(111) for each of the three structures.

The p(2x2) structure on both Rh and Pt appears to be incapable of ethyl group ordering, since the PPE curves (Fig. 6) are very flat and show no clear minima. Free rotation of the CH$_2$CH$_3$ group is predicted irrespective of temperature (room temperature corresponds to about 0.5 kcal/mole); this is in agreement with experimental findings for propylidyne on Rh(111) for temperatures in the range 230-270 K, on Pt(111) in the range 280-400 K and for propylidyne on Pt(111) in the range 350-400 K.

The c(4 x 2) structure is more stable, with respect to rotational disorder-

ing, than the (2 x 2) structure; both on Rh and Pt a minimum in PPE appears, although it is at least 60° wide, which still means substantial rotational freedom. However, the c(4 x 2) structure can be formed experimentally from the (2 x 2) one for propylene on Rh(111) on increasing the temperature above 270 K. The PPE's being almost the same, one would be inclined to think that the occurrence of transition is due to entropy effects whose detailed analysis is beyond the scope of the present work. On the whole, it can be said that ethyl group ordering may be easier for c(4 x 2) than for (2 x 2), but still difficult on Rh or Pt: it is possible that a metal with a shorter (111) nearest neighbor distance would allow a more closely-packed (and stable) c(4 x 2) over-layer to form. This trend is, at least, consistent with the observation that c(4 x 2) forms on Rh and does not on Pt. Nevertheless, there is no experimental evidence of methyl group ordering in the c(4x2) structure; cooperative rotation being hindered by a barrier of 7 kcal/mole, a possible explanation of this is in terms of single-molecule jumps between the two potential energy wells seen in Figure 7, through a barrier that does not exceed 3.5 kcal/mole.

The (2√3 x 2√3)R30° structure is the most likely to be ordered on both metals in the sense of having a preferred angle of simultaneous rotation of the three molecules in Figure 5. The PPE curves have narrow minima with steep walls, since the threefold axes bring the methyl groups in close contact. This is seen on both Rh and Pt, so that it is suggested that this structure may form also on Pt, given the right temperature-coverage range. Figure 8 shows that the best (111) metal spacing to obtain a close-packed (2√3 x 2√3)R30° structure is d ~ 2.60, quite near to the Rh spacing: this example illustrates another predictive capability of the monolayer packing energy method, that is, given any desired overlayer structure, to determine the best spacing (and hence the best metal substrate) that will accommodate it on steric grounds.

Since CH_3 groups come in close contact on this θ rotation, methyl group rotation about its own axis by an angle χ can become important also. The energy profiles must, thus, become two-dimensional energy surfaces, as a function of the two torsion angles. The total energy variation during methyl rotation must also include all intramolecular energy terms, however; the ethane-like barrier

$$E(intra) = \frac{E^\circ}{2} \cos(1 - 3\chi), \quad E^\circ = 3 \text{ kcal/mole}$$

has tentatively been used: Figure 9 shows the resulting map. In this respect, it may be noted that our assumption that the adsorbate-surface energy remains constant includes the (very reasonable) consequence that no torsional energy is associated with rotation about the C-CH_2 bond in propylidyne. The crude approximation due to use of the ethane-like barrier prevents us from making quantitative predictions as to the best values of θ and χ. What can be confidently stated is that the true minimum must be along the line connecting the two minima in Figure 9; the methyl C's point more towards each other and the methyl H's rotate away from the staggered configuration to avoid short contacts.

As we mentioned earlier, a LEED structural determination gives a rotation angle of $\theta = 30°$. This corresponds to the largest angle of rotation compatible with nonoverlapping Van der Waals spheres, if one allows the methyl groups to rotate about their axis by about $45°$ from the staggered configuration. This geometry has the largest possible number of H-H contacts between molecules, namely three per pair of touching molecules and thus nine contacts per cluster of three touching molecules. This result would be in agreement with the PPE calculations if there were no intramolecular torsional barrier.

The same calculations as for propylidyne were repeated for butylidyne on Rh and Pt. In this case there are, in fact, three torsional degrees of freedom, but terminal methyl group rotation was considered to be less relevant, since the

three H atoms point essentially upwards, and away from intermolecular contacts.
The angle χ carries over to the case of butylidyne with the same definition:
in this case, its variation causes rotation of a staggered ethyl group. In the
absence of any better hypothesis concerning the torsional barrier, the same
threefold potential as for propylidyne was used. The results for butylidyne
closely parallel those for propylidyne; Figure 10 is analogous to Figure 6, and
a θ/χ surface essentially similar to that shown in Figure 9 is obtained. One
important difference is the finding that in the $(2\sqrt{3} \times 2\sqrt{3})R30°$ structure the
terminal ethyl groups point away from each other (see Figure 11). For butyli-
dyne, the three possible structures also differ more markedly in energy, the
order of stability being

$$p(2 \times 2) < c(4 \times 2) < (2\sqrt{3} \times 2\sqrt{3})R30°$$

This confirms that the $(2\sqrt{3} \times 2\sqrt{3})R30°$ structure is certainly the most tightly
packed one, an effect that is more and more clearly visible as the size of the
molecule increases.

As in the case of propylidyne, it is seen (Figure 10) that no ordering of
ethyl groups in the p(2 x 2) structures is possible, which is again in agree-
ment with LEED observations. The ethyl groups in the $(2\sqrt{3} \times 2\sqrt{3})R30°$ structure
are found to be ordered, as would be expected from the shape of the potential
energy minimum. The hydrocarbon chains are, however, (Figure 11) not strictly
zig-zag (all trans) and parallel, as they are known to be in pure alkane crystals,
and the surface cell spacing, even in the most closely packed structure, is
larger than the ideal chain-to-chain separation in an actual alkane crystal:
cell edges perpendicular to the direction of chain elongation are 4.2 and 4.8Å
for a typical alkane crystal (see discussion in Ref. 2b and references therein).

Another illustration of possible uses of the monolayer packing energy method

is provided by the case of methylacetylene. (A reasonable structure for the surface methylacetylene molecule was derived from analogies with organometallics,[7] see Figure 12c). The most stable p(2 x 2) structure for this molecule is in fact that of Figure 12a. From LEED experiments, the methyl group appears, however, to be disordered, since its contribution to the total scattered intensity is negligible and the I-V curves are similar to those for acetylene. The arrangement shown in Figure 12b, in which H and CH_3 have been interchanged for a single molecule of methylacetylene in the overlayer, has a very high potential energy. The disorder cannot, therefore, be due to 180° rotation around the perpendicular to the triple bond. As Figure 13 shows, there is a much easier mechanism by which the ethyl group can disorder--that is, by rotation around the triple bond itself. Especially on Pt, such a rotation is seen to be very easy as regards adsorbate-adsorbate energy, and there is a good chance that such a rocking motion does not cause significant perturbations to the carbon-surface bond (such a rocking motion would of course be limited to a certain angular range). This conclusion would be quite consistent with that derived from LEED.

4. CONCLUSIONS

Our main finding is that the predictions of force-field calculations are to a large extent compatible with predictions from studies by LEED and other surface sensitive techniques, in the case of C_3 and C_4 hydrocarbons adsorbed on Pt and Rh(111) single crystal surfaces.

Specifically, it appears that the ethyl group in propylidyne on these surfaces can be rotationally disordered (about the surface normal) at room temperature in the observed p(2 x 2), c(4 x 2) and $(2\sqrt{3} \times 2\sqrt{3})R30°$ structures at 1/4 monolayer coverage (but in the latter structure all ethyl groups should

rotate in phase to produce the observed pattern). Also, the propyl group in butylidyne on Pt(111) can be disordered in the same way in the $(2\sqrt{3} \times 2\sqrt{3})R30°$ structure. The methyl group in methylacetylene parallel-bonded to Pt(111), which is thought to be bent away from the C≡C axis, can azimuthally disorder, but the molecule can not rotate by 180° about the surface normal.

It is also clear from our model calculations that smaller surface unit cells than those observed by LEED cannot exist for these molecules because of steric hindrance.

One question remains unanswered: why will propylidyne produce a $(2\sqrt{3} \times 2\sqrt{3})R30°$ structure on Rh(111) and not on Pt(111) and why will butylidyne produce such a structure on Pt(111) and not on Rh(111)?

ACKNOWLEDGMENTS

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   C_3 and C_4 hydrocarbon studies on Pt(111) and Rh(111) appear in:

   i) R.J. Koestner, J.C. Frost, P.C. Stair, M.A. Van Hove and G.A. Somorjai, to be published.

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FIGURE CAPTIONS

Figure 1: Ethylidyne species ordered on fcc(111) metal substrates. The p(2 x 2) ordering occurs on both Pt(111) and Rh(111), while the c(4 x 2) structure is only observed on Rh(111). There is some uncertainty concerning the latter structure (see text). The sphere diameters have no physical significance.

Figure 2: A possible bonding arrangement for methylacetylene on Pt and Rh(111). The methyl group and the lone hydrogen are tilted away from the surface, while the C-C bond parallel to the surface may have double-bond character.

Figure 3: Three alkylidynes on fcc(111), drawn with the staggered configuration within each molecule.

Figure 4: View down onto the surface of a $(2\sqrt{3} \times 2\sqrt{3})R30°$ propylidyne structure with staggered intramolecular configurations. This structure corresponds to the rotation angle $\theta = 0°$ (see text). A unit cell is delineated. Top part uses Van der Waals radii for the hydrogen atoms, while bottom part shows the skeletal structure.

Figure 5: Contents of unit cell of the propylidyne structure shown in Figure 4.

Figure 6: Packing potential energy for propylidyne on Pt(111) and Rh(111). The dimensions of the propylidyne unit and definition of the rotation angle θ are also shown. All the molecules in the structure rotate in phase.

Figure 7: Same as Figure 6, but only one molecule rotates in a fixed environment.

Figure 8: a) PPE curves for propylidyne on different surfaces for the $(2\sqrt{3} \times 2\sqrt{3})R30°$ structure. Angle θ as in Figure 6. b) The PPE of this structure as a function of d(111) metal spacing.

Figure 9:   Potential energy maps for $(2\sqrt{3} \times 2\sqrt{3})R30°$ propylidyne on Pt and Rh(111).
             Isoenergetic curves at 0.5 kcal/mole intervals. Definition of θ and
             χ angles is shown. The full dot shows the minimum in packing energy,
             the triangle, the minimum in total potential energy (packing + torsional).
             Dashed areas are regions of high potential energy.

Figure 10:   Same as Figure 6 for butylidyne.

Figure 11:   Views in projection onto the surface of propylidyne and butylidyne.
             C_3 indicates a threefold rotational axis. a) Propylidyne,
             $(2\sqrt{3} \times 2\sqrt{3})R30°$: the most stable conformation has $\theta >$
             0, $\chi < 0$, one methyl hydrogen points toward its neighbor. b)
             Butylidyne, same structure: $\theta > 0$, $\chi > 0$ bring the ethyl groups
             around the threefold axis away from each other.

Figure 12:   a) The most stable structure for an overlayer of methylacetylene
             on Pt or Rh(111). b) When one molecule is rotated by $180°$ a
             sharp destabilizaton occurs. c) Methylacetylene geometry used in
             the calculation is also shown.

Figure 13:   Full line: PPE for oscillation of $HCCCH_3$ around the axis perpendi-
             cular to the triple bond. Broken line: same for "tumbling" oscil-
             lation around an axis coincident with the triple bond. The zero of
             both oscillation angles corresponds to the structure shown in Figure
             12a.

c(4×2)

p(2×2)
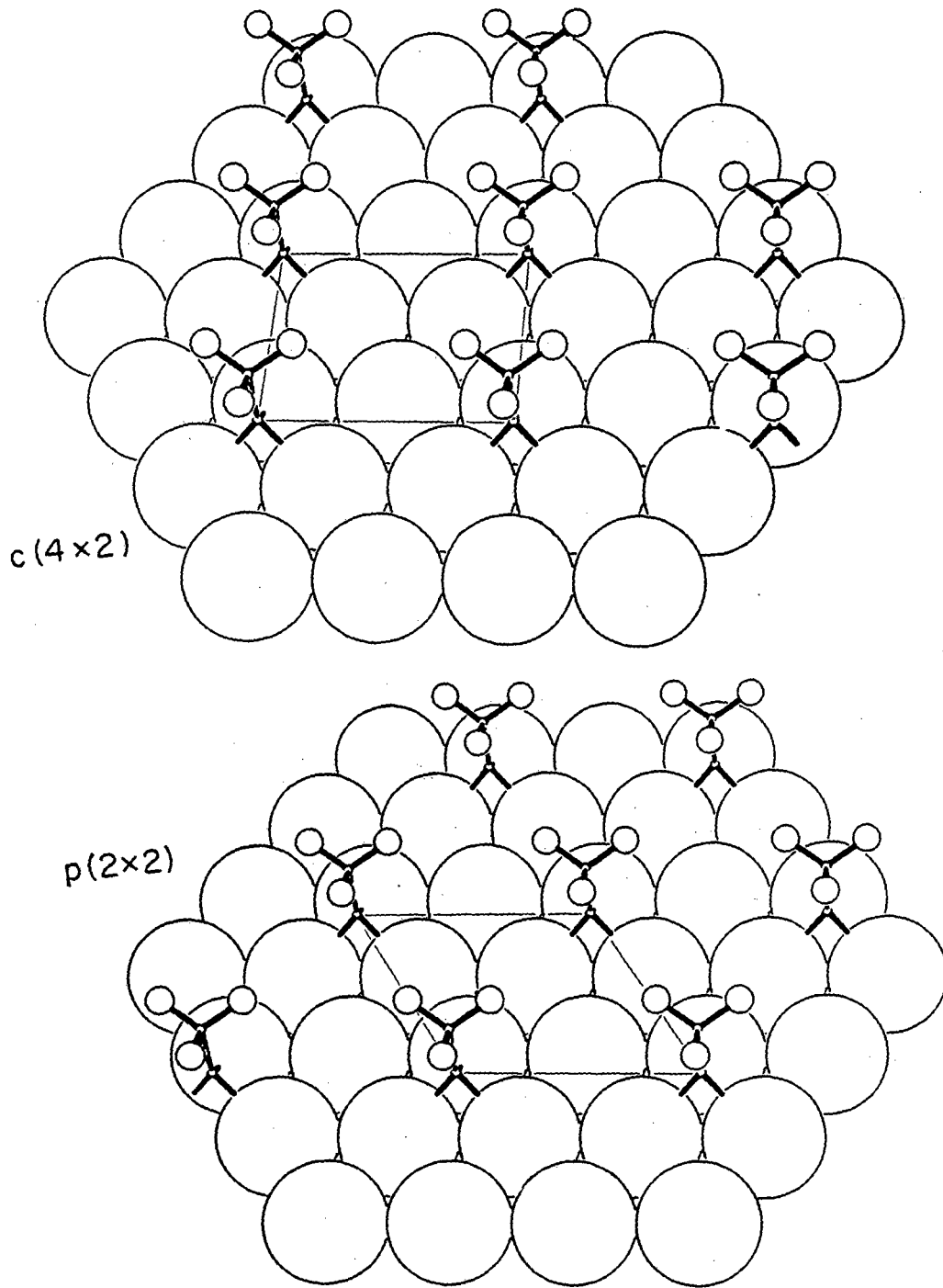
fcc (III) + C$_2$H$_3$ (ethylidyne)

XBL813-5407

Fig. 1

Methyl group is
randomly attached
to either carbon atom
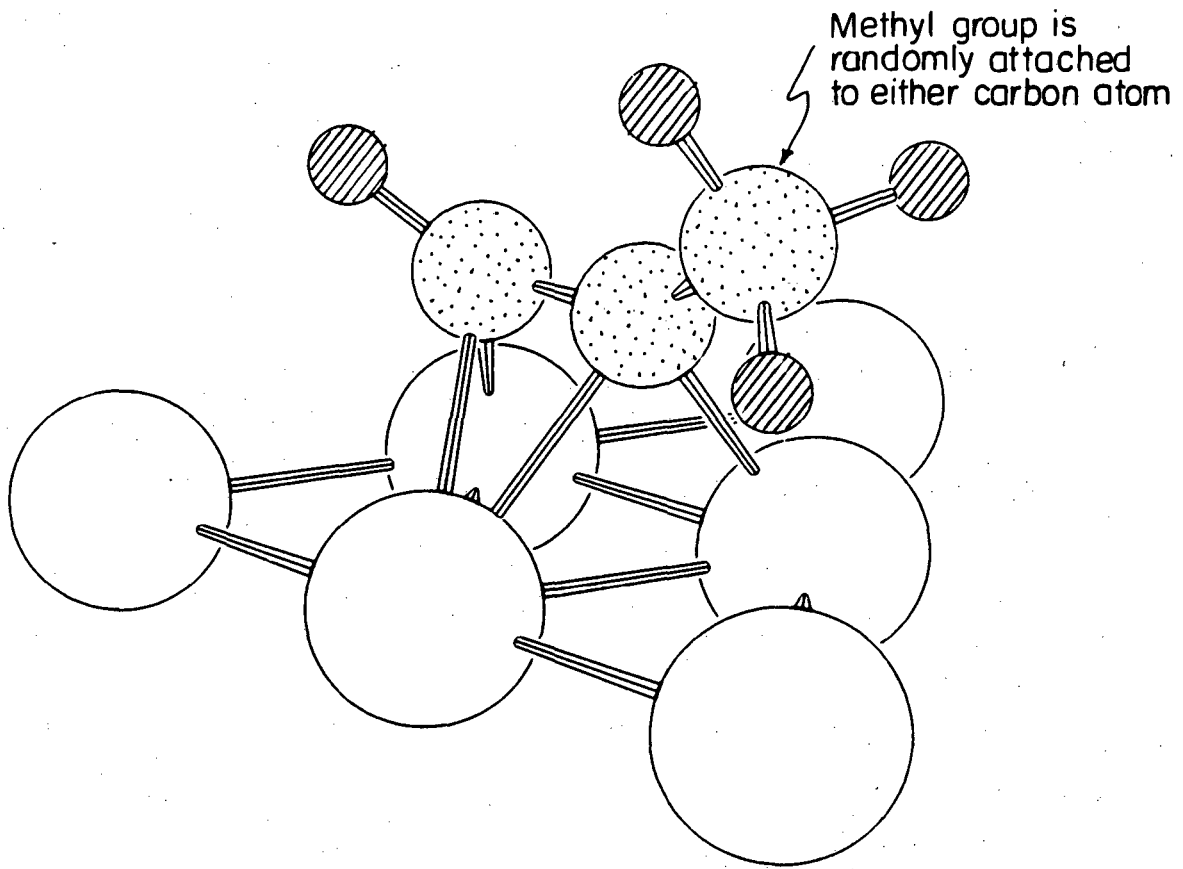
Metastable methylacetylene on Pt(III)

XBL 817-6067

Fig. 2
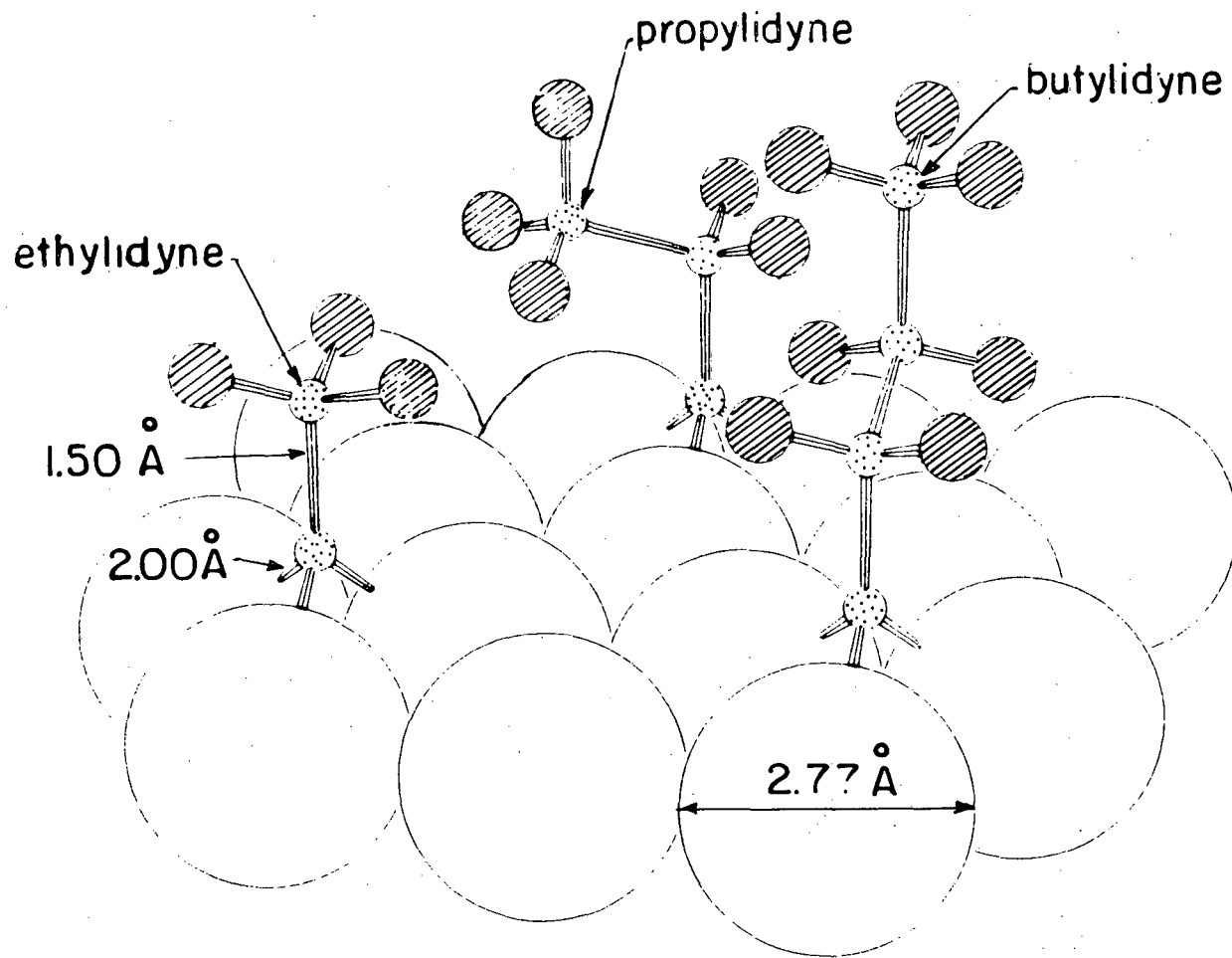
Pt (III) + ethylidyne, propylidyne and butylidyne

Fig. 3

XBL 8110-6882
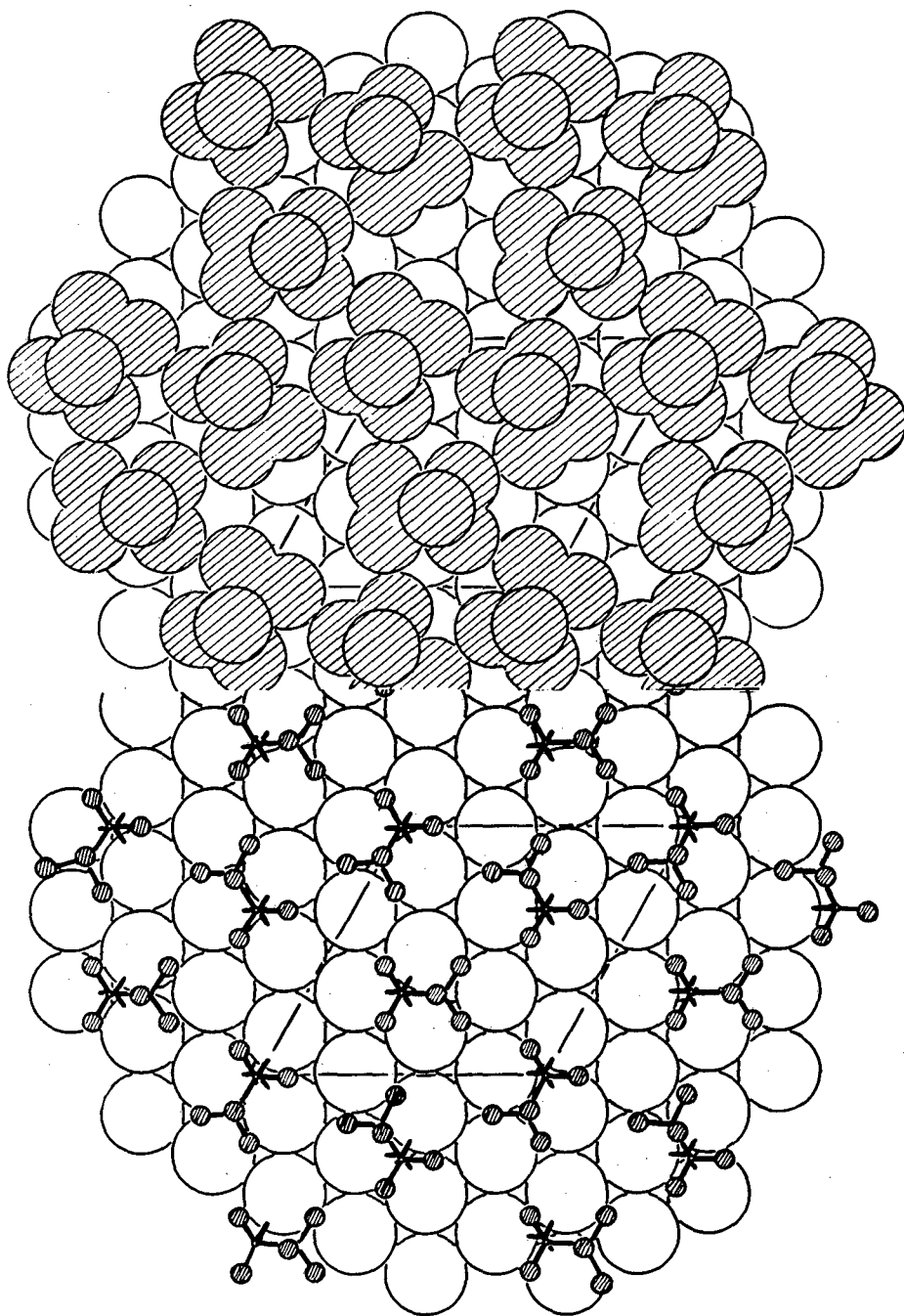
fcc (III) + $(2\sqrt{3} \times 2\sqrt{3})$ R30° C_3H_5 (propylidyne)

XBL 813-5410

Fig. 4
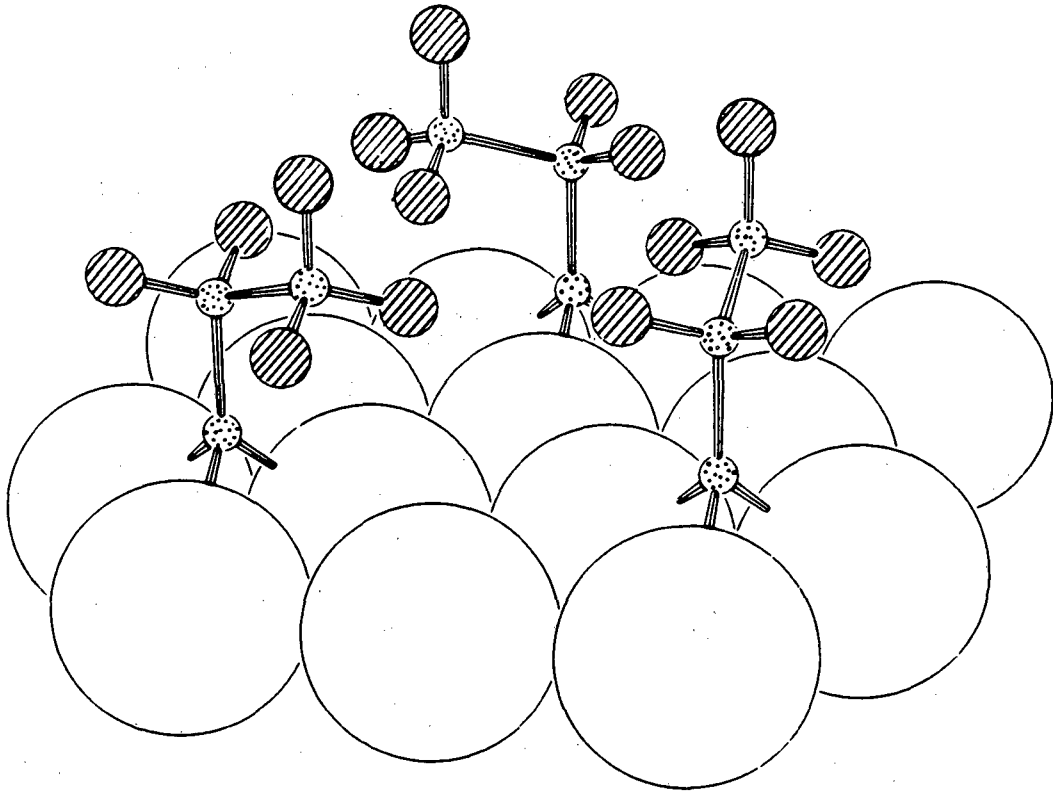
fcc (III) + C$_3$H$_5$ (propylidyne)

XBL 817- 6065

Fig. 5
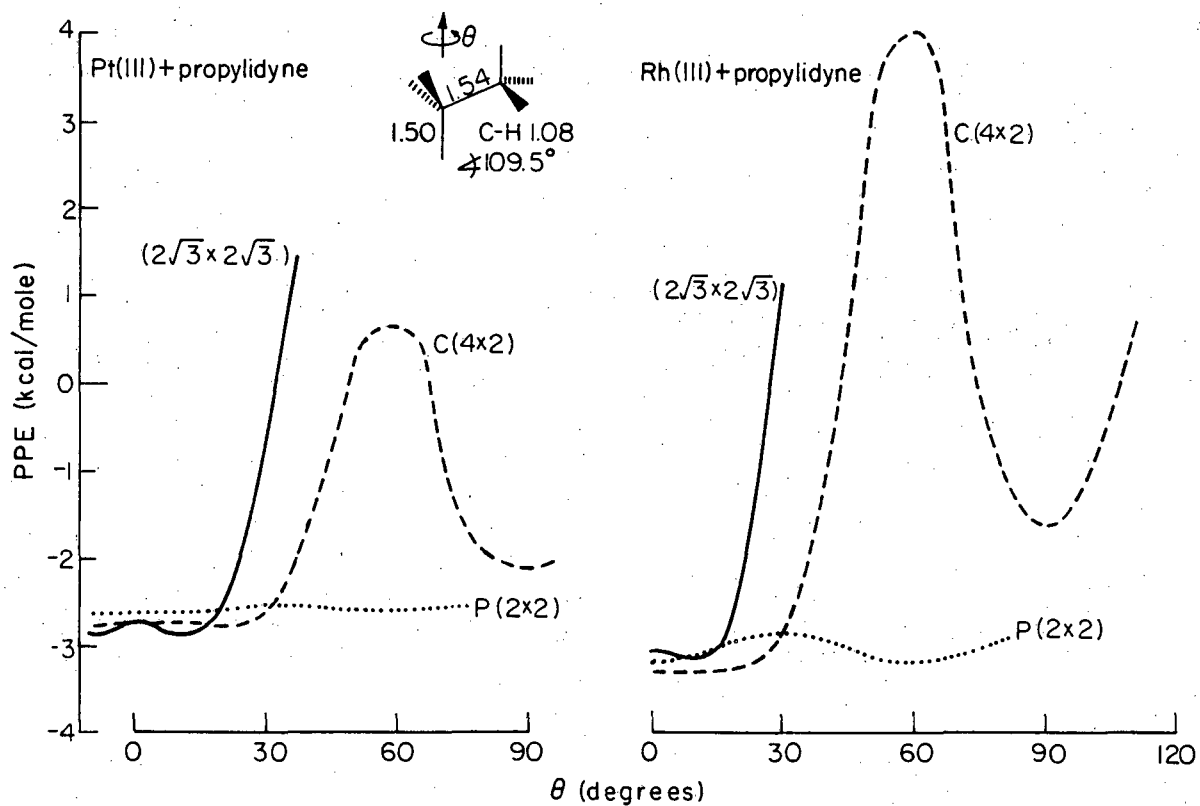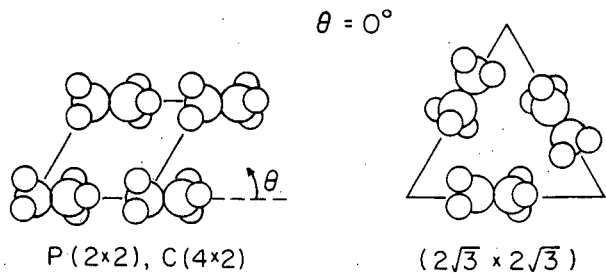
Fig. 6
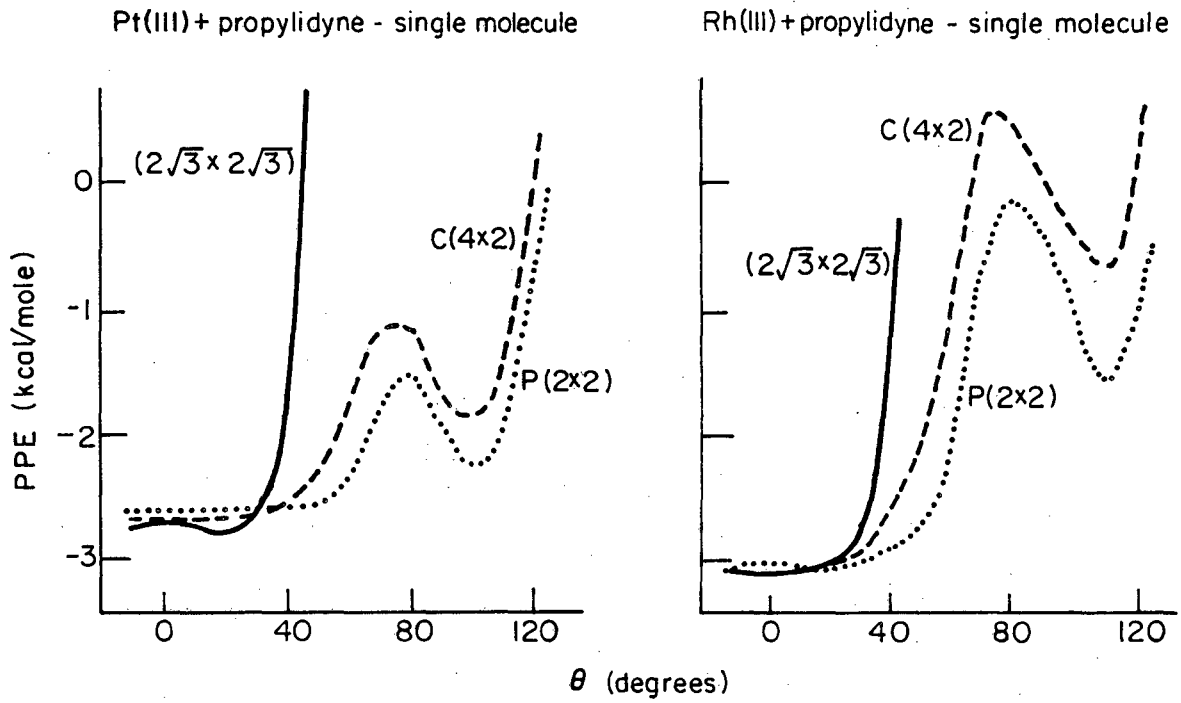
Fig. 7

$$2\sqrt{3} \times 2\sqrt{3}$$
metal + propylidyne
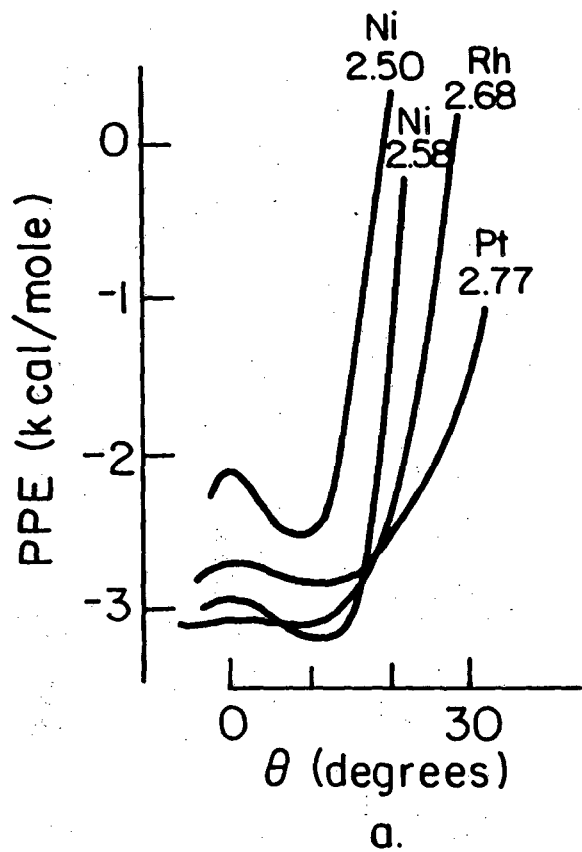
d = metal-metal spacing
on fcc (III)

a.

Fig. 8

b.
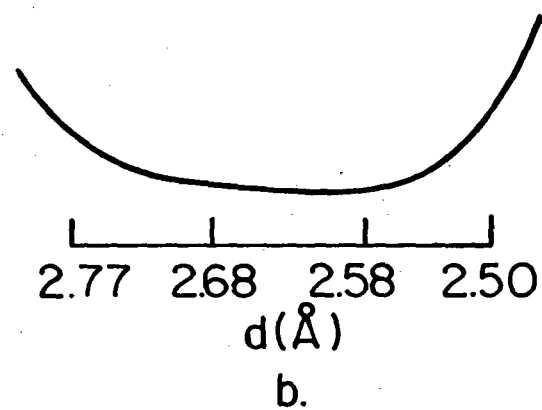
XBL 822-5235

PROPYLIDYNE $(2\sqrt{3} \times 2\sqrt{3})$

XBL 822–5236

Fig. 9

Fig. 10

-26-
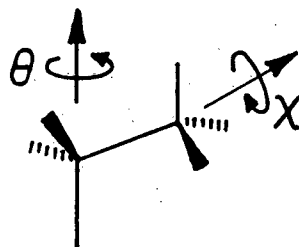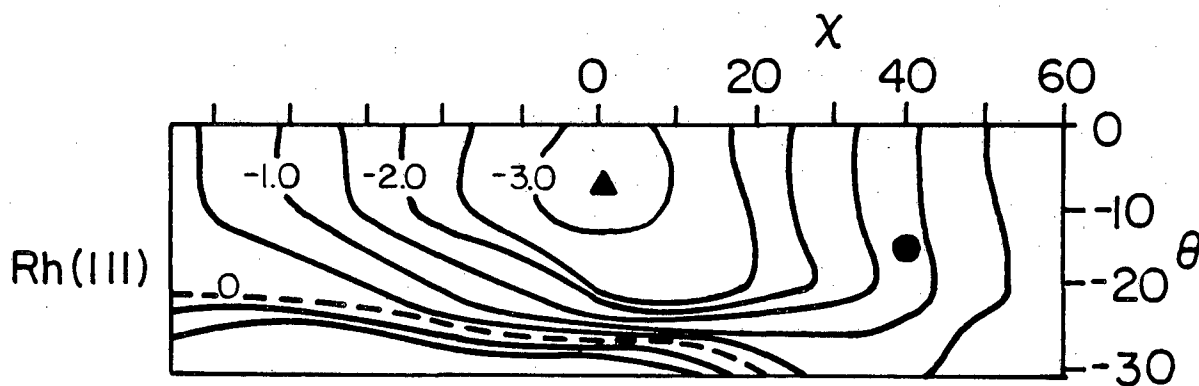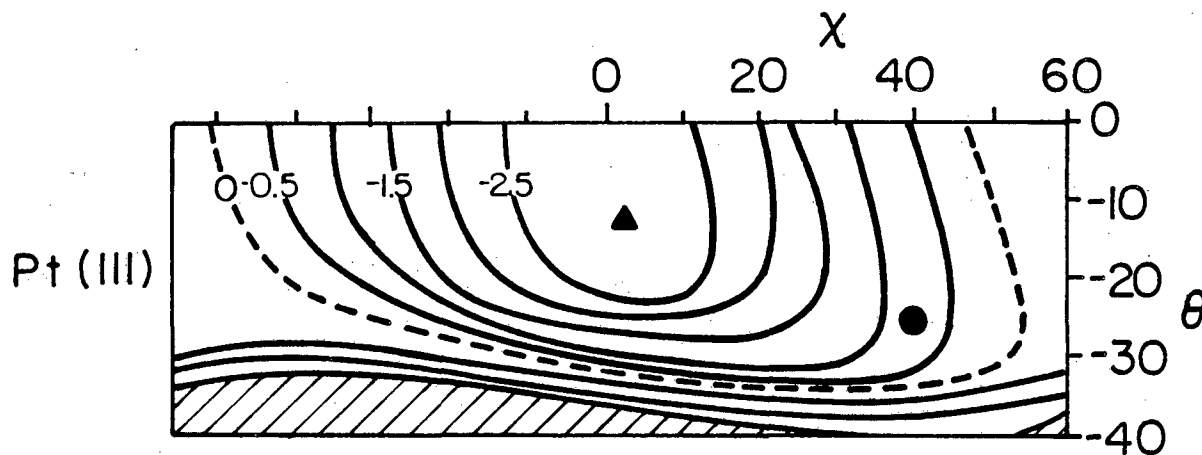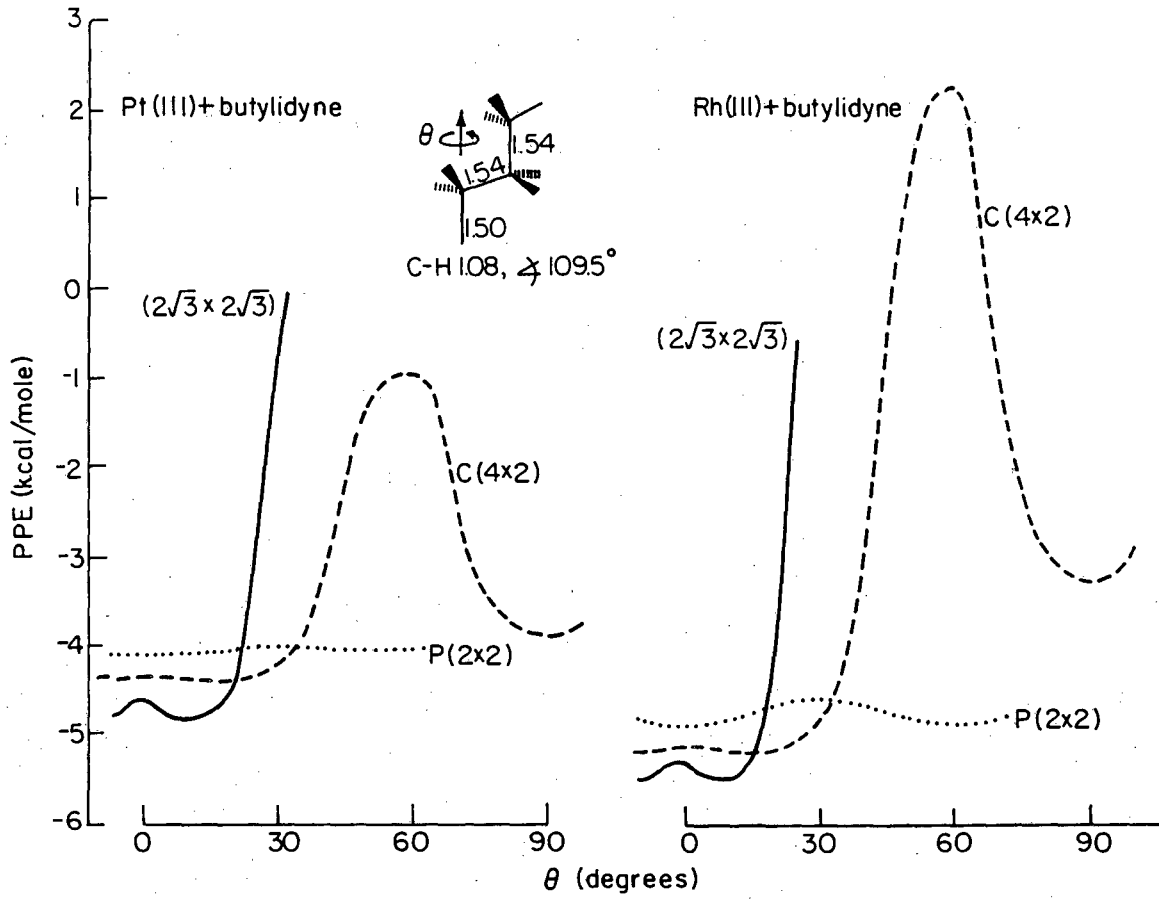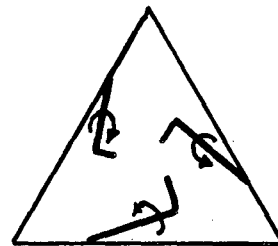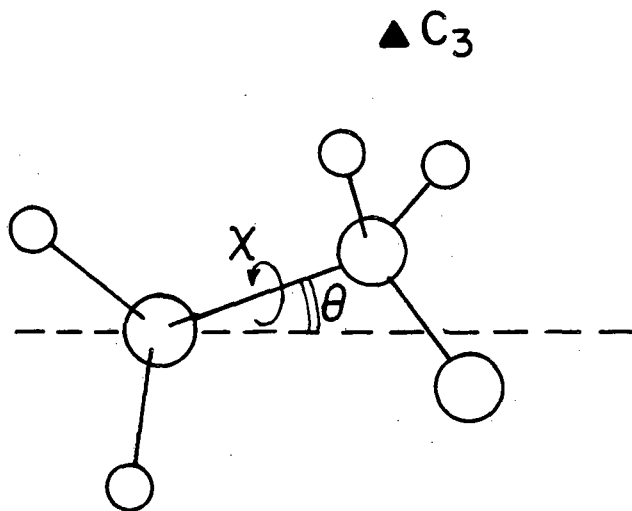
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a.
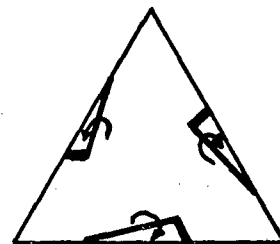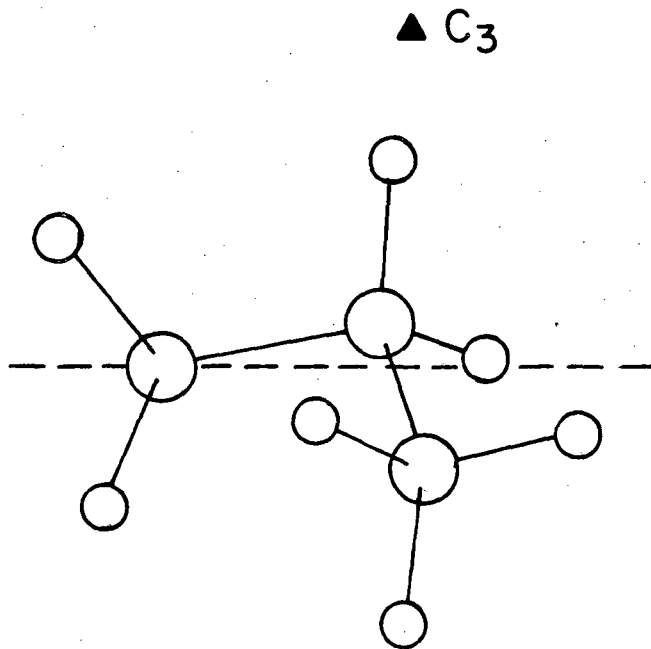
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b.

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Fig. 11
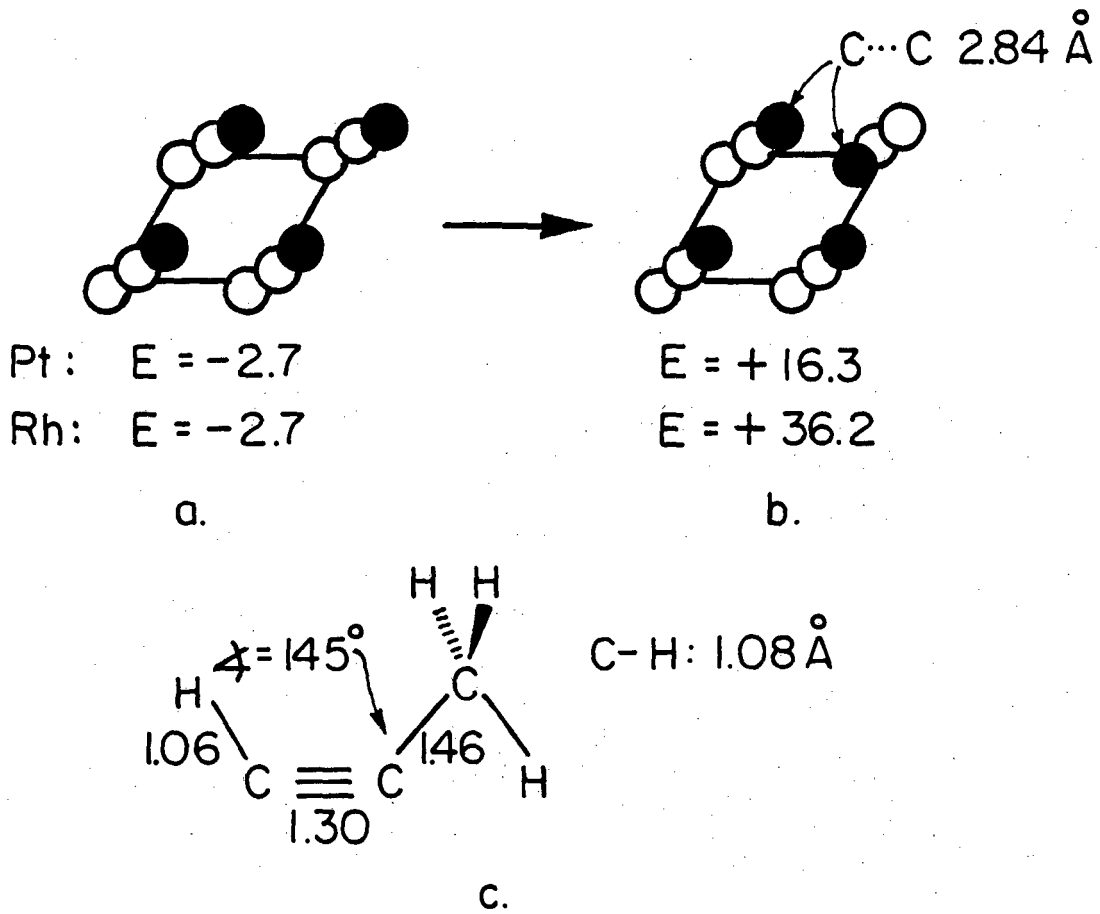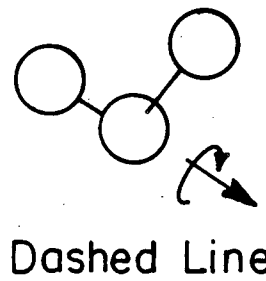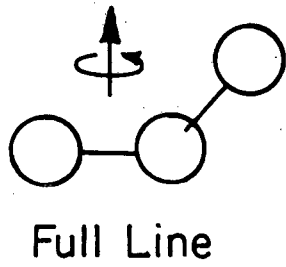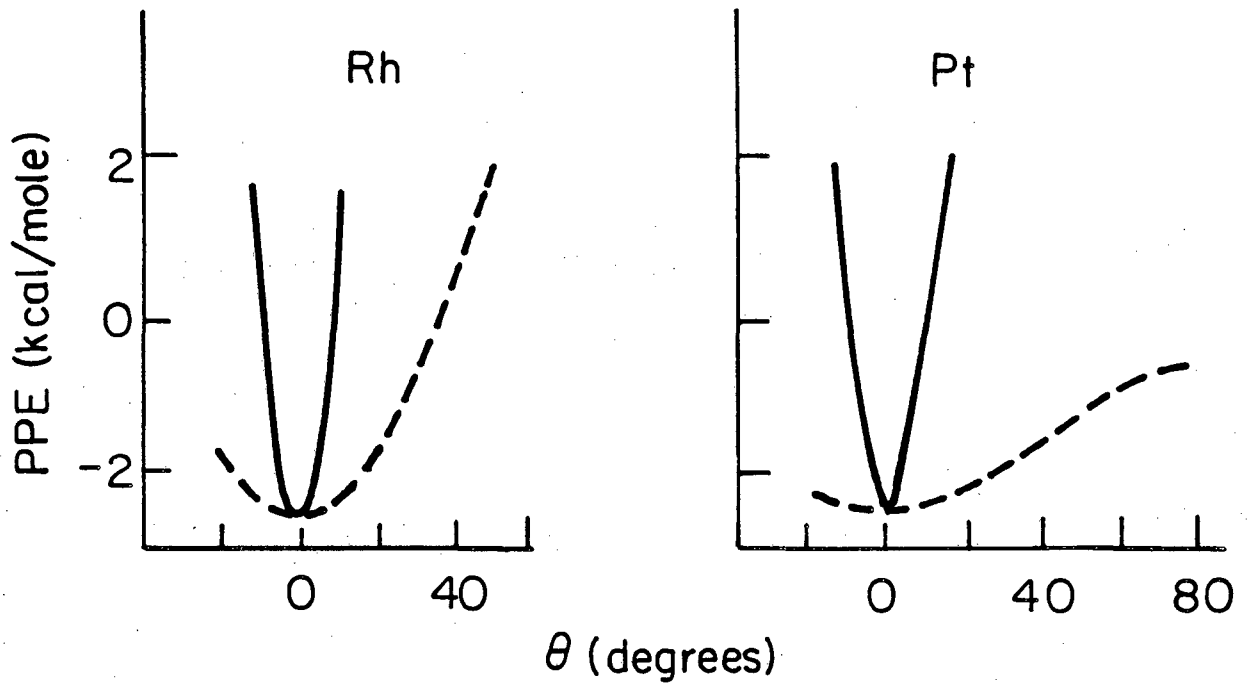
Fig. 12

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Fig. 13

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