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TRIPLET ELECTRONIC GROUND STATE OF TRIMETHYLENEMETHANE*

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ABSTRACT

A nonempirical quantum mechanical study of the electronic structure of $C(CH_2)_3$ has been carried out. A double zeta basis set of contracted gaussian functions was employed, and self-consistent-field wave functions obtained for the triplet ground state. The planar (D_{3h}) configuration is predicted to lie 17 kcal/mole below the orthogonal (C_{2v}) form. The electronic structure is discussed in terms of Mulliken populations and orbital perspective plots. Some preliminary results for the lowest singlet states are reported.

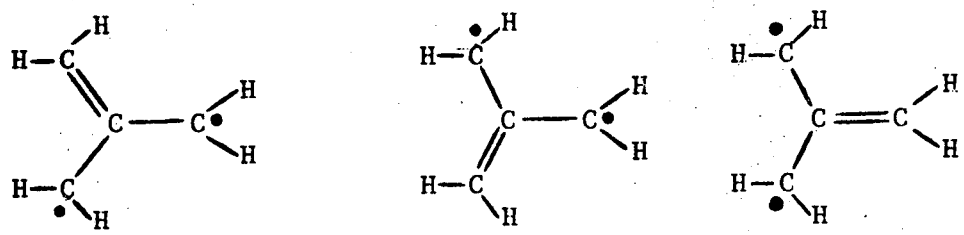
*Work performed under the auspices of the U.S. Atomic Energy Commission.

**Charles Fish Fellow.

***Alfred P. Sloan Fellow.

INTRODUCTION

There is a long history of interest among theoretical organic chemists in the trimethylenemethane radical, traditionally represented by the three structures



(1)

Interest in $C(CH_2)_3$ began in 1948 with the work of Moffitt, who was cited in a paper by Coulson[1] as having shown the central atom in trimethylenemethane to have the greatest π bond order attainable by a carbon atom. In a related paper appearing four years later, Greenwood[2] discussed the critical role of $C(CH_2)_3$ in the notion of "free valence", defined by Coulson[1]

$$F.V. = N_{max} - N \tag{2}$$

where N is the total bond order of the atom in question. N_{max} is the maximum possible bond order, $3 + \sqrt{3}$, the value taken on by the central atom of trimethylenemethane. Hence the free valence of the central carbon $(C(CH_2)_3$ is identically zero and serves as a frame of reference.

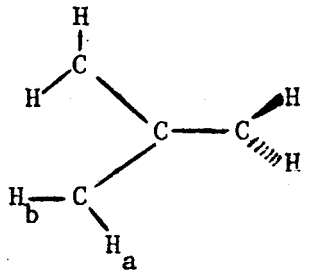
The role of trimethylenemethane as one of the simplest hydrocarbon molecules possessing no normal Kekule-type structure was first discussed by Longuet-Higgins[3] in 1950. The general question he addressed was "why are there relatively few stable molecules for which it is impossible to write some classical valence bond structure?" At the time, of course, $C(CH_2)_3$ was no more than a gleam in the eyes of several theoreticians. Using qualitative molecular orbital theory, Longuet-Higgins was able to show that such non-Kekule molecules should have paramagnetic ground states, react extremely easily with oxygen, and hence be very difficult to prepare in the presence of air.

Trimethylenemethane has also played an important role in the development of the theory of zero field splittings in organic triplet states. The first paper in this area was that of McConnell,[4] who predicted a negative spin density at the central carbon atom and suggested that the spin-spin parameter D might be close to zero. A longer paper[5] by McLachlan on the same problem appeared shortly thereafter, and considered, but ultimately discounted, the possibility that D for $C(CH_2)_3$ might take on a negative value. More detailed calculations of the zero field splittings have recently been reported by Gold[6] and by Gondo and Maki.[7]

Among the most sophisticated of the semi-rigorous calculations performed on $C(CH_2)_3$ are those of Chong and Linnett, who compared the methods of alternate molecular orbitals[8] and non-paired spatial orbitals.[9]

In light of the above theoretical background, the importance of the first preparation of trimethylenemethane by Dowd[10] is obvious. The original synthesis was by irradiation of the pyrazoline system . Experimental work following this initial breakthrough has been nicely summarized in a recent review article by Dowd.[11] Of particular importance to us is the electron diffraction study[12] of the related compound $C(CH_2)_3Fe(CO)_3$. The C-C bond distance was found to be 1.437 Å and the C-H distance 1.111 Å. Also noteworthy is the photoelectron spectrum of the same compound, obtained by Dewar and Worley.[13]

The recent semi-empirical study of Dewar and Wasson[14] differs in scope from earlier theoretical work, in that the potential energy surfaces of the three lowest electronic states were explored. As expected, the planar triplet state is predicted to be the electronic ground state. However, the first excited state is an open-shell singlet, predicted to have one methylene group orthogonal to the other two.



(3)

This result appears to be consistent with the conclusions of Doering and Roth,[15] based on the stereochemistry of the methylenecyclopropane rearrangement.

A final index of the impact of trimethylenemethane is the significant number of texts in which it is used as an example.[16]

In the present paper we present the first a priori study of the electronic structure of $C(CH_2)_3$. A primary goal is to discuss the electronic structure of the planar triplet state in terms of population analyses and perspective plots. We also discuss the lowest planar singlet state, as well as the triplet ground state in its orthogonal configuration.

THEORETICAL ASPECTS

For planar D_{3h} geometries, the lowest electron configuration of trimethylenemethane is

$$1a_1'^2\ 1e'^4\ 2a_1'^2\ 3a_1'^2\ 2e'^4\ 4a_1'^2\ 3e'^4\ 1a_2'^2\ 4e'^4\ 1a_2''^2\ 1e''^2 \qquad (4)$$

Hence we expect the ground state to be $^3A_2'$, the first excited state to be $^1E'$, and the second excited state to be of $^1A_1'$ symmetry.

If we retain the D_{3h} nuclear geometry, but require the individual orbitals to transform according to the lower symmetry point group C_{2v}, we now have three electron configurations

$$1a_1^2\ 2a_1^2\ 1b_2^2\ 3a_1^2\ 4a_1^2\ 5a_1^2\ 2b_2^2\ 6a_1^2\ 7a_1^2\ 3b_2^2\ 4b_2^2\ 8a_1^2\ 5b_2^2\ 1b_1^2\ 1a_2\ 2b_1 \quad {}^3B_2,\ {}^1B_2 \qquad (5)$$

$$\frac{1}{\sqrt{2}}\ 1a_1^2\ 2a_1^2\ 1b_2^2\ 3a_1^2\ 4a_1^2\ 5a_1^2\ 2b_2^2\ 6a_1^2\ 7a_1^2\ 3b_2^2\ 4b_2^2\ 8a_1^2\ 5b_2^2\ 1b_1^2\ 1a_2^2$$

$$\pm\frac{1}{\sqrt{2}}\ 1a_1^2\ 2a_1^2\ 1b_2^2\ 3a_1^2\ 4a_1^2\ 5a_1^2\ 2b_2^2\ 6a_1^2\ 7a_1^2\ 3b_2^2\ 4b_2^2\ 8a_1^2\ 5b_2^2\ 1b_1^2\ 2b_1^2 \quad {}^1A_1 \qquad (6)$$

The correspondence between D_{3h} and C_{2v} electronic states is[17]

$$^3A_2' \rightarrow {}^3B_2$$

$$^1E' \rightarrow {}^1B_2 + {}^1A_1$$

$$^1A_1' \rightarrow {}^1A_1 \qquad (7)$$

For D_{3h} geometries, the symmetric combination of configurations (6) will be of $^1A_1'$ irreducible representation, while the antisymetric combination will be a $^1E'$ state.

One might think that the total self-consistent-field (SCF) energy of the $^1E'$ state should be the same whether it is obtained using configuration (4), configuration (5), or the antisymmetric combination of configurations (6). However, this is not the case.[18] In fact, the imposition of full D_{3h} symmetry upon the orbitals represents a significant constraint on the SCF wave function of this open-shell system. Furthermore, even when the calculations are carried out for C_{2v} orbitals, the $^1B_1$ and $^1A_1$ components of the ^1E state are not precisely degenerate. This latter inconsistency illustrates the equivalence restrictions problem discussed by Julienne, Krauss, and Wahl[19] with reference to the asymptotic degeneracy of the $^2\Pi$ and $^2\Sigma^+$ states of HF^+. Finally it should be noted that semi-empirical methods suffer from similar inconsistencies. For example, the MINDO calculations of Dewar and Wasson[14]

predict, in the limit of D_{3h} geometry, the $^1B_2$ state to lie a full 20 kcal/mole below the $^1A_1$ state. In fact, of course, these two states are the degenerate components of the $^1E'$ state.

Our next problem is to correlate the D_{3h} electronic states with those for the nonplanar orthogonal geometry (3). As the nonequivalent methylene group is twisted out of the plane, only a single twofold rotation remains, and hence the new point group is C_2. The overall state symmetries of twisted trimethylenemethane are determined by the symmetries of the open-shell orbitals, which resolve as

$$\begin{array}{l} \quad\quad\quad\quad 1a_2 \longrightarrow 9a \\ 1e'' \\ \quad\quad\quad\quad 2b_1 \longrightarrow 7b \end{array} \tag{8}$$

Therefore the $C_{2v} \rightarrow C_2$ state correlation is

$$^3B_1 \rightarrow {}^3B \qquad\qquad {}^1B_1 \rightarrow {}^1B \qquad\qquad {}^1A_1 \rightarrow {}^1A \tag{9}$$

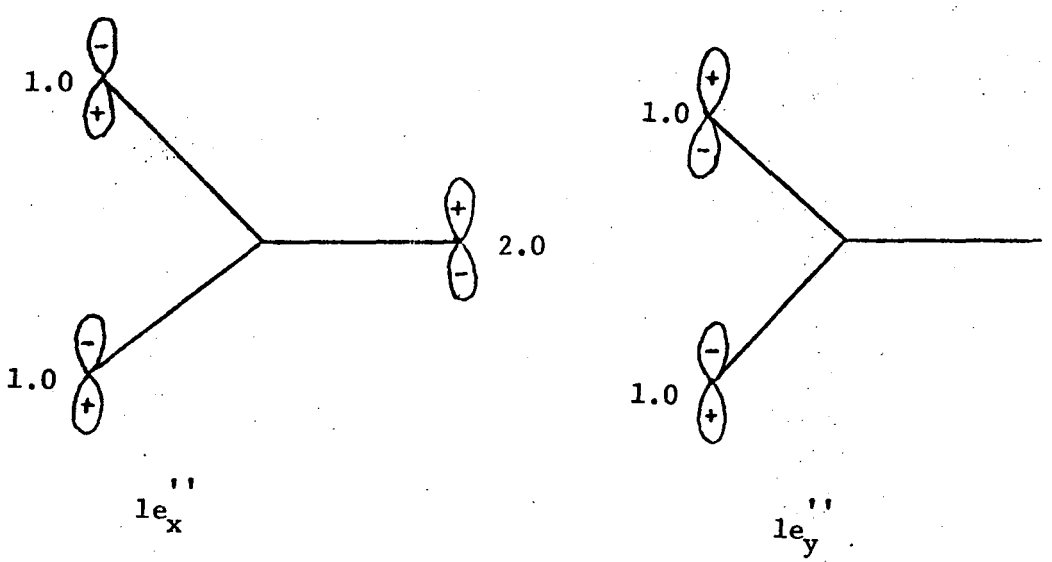
When we proceed from the twisted form to the orthogonal geometry (3), the point group changes from C_2 to C_{2v}. Unfortunately, we then have the ambiguous correlation

$$a \rightarrow a_1 \text{ or } a_2 \; ; \; b \rightarrow b_1 \text{ or } b_2 \quad . \tag{10}$$

Hence there are four acceptable (from symmetry considerations only) sets of electron configurations: a_1^2, b_1^2, $a_1\, b_1$; or a_1^2, b_2^2,

a_1b_2; or a_2^2, b_1^2, a_2b_1; or, finally, a_2^2, b_2^2, a_2b_2, where only the outer two electrons have been indicated. Which of these four sets of configurations will correlate with the $1e''^2$ configuration of D_{3h} trimethylenemethane cannot be determined by symmetry arguments alone. In fact, the correct adiabatic correlation can only be made by knowing the relative positions of the various electronic states in the orthogonal configuration.

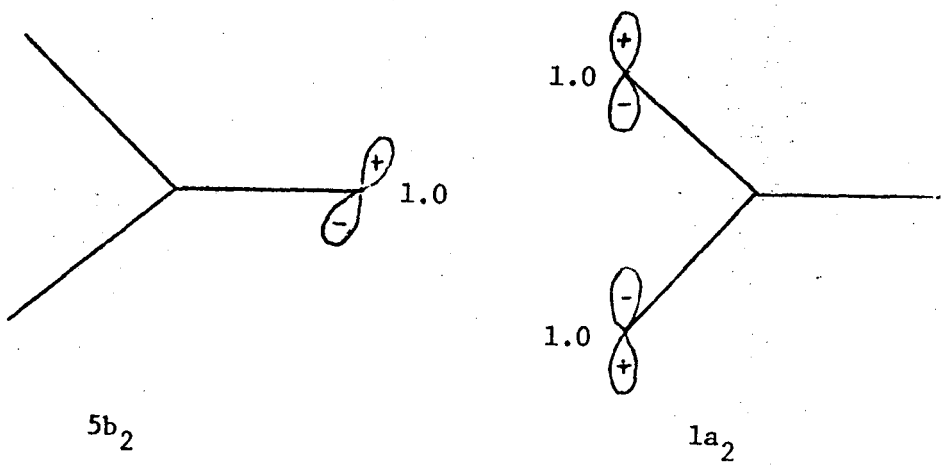
However, simple orbital considerations can guide us to a reasonable prediction of the correct state correlation. For the planar triplet, the two components of the $1e''$ orbital may be depicted as



(11)

In these sketches, the lobes of the $p\pi$ orbitals are meant to lie above and below the plane of this page. When the molecule is twisted into the orthogonal form (3), the $1e_y''$ remains intact, but is now the $1a_2$ orbital. The $1e_x''$ combination is no longer

a symmetry orbital, but is likely to be converted (during the adiabatic twisting motion) to a distorted atomic p function perpendicular to the function with coefficient 2.0 in the $1e_x''$ orbital of (11). That is the orbitals of (11) are likely to correlate with the orbitals



(12)

Hence the electron configuration for orthogonal trimethylenemethane should be

$$1a_1^2\ 2a_1^2\ 1b_2^2\ 3a_1^2\ 4a_1^2\ 5a_1^2\ 2b_2^2\ 6a_1^2\ 7a_1^2\ 3b_2^2\ 1b_1^2\ 4b_2^2\ 8a_1^2\ 2b_1^2\ 5b_2\ 1a_2 \qquad (13)$$

In the present study we have carried out <u>ab initio</u> SCF calculations on the planar $^3A_2'$, $^1E'$, and $^1A_1'$ states arising from electron configuration (4). To test the effects of the spatial symmetry restrictions implicit in (4), the same electronic states have been studied with orbitals constrained only to be of C_{2v} symmetry. That

is, SCF wave functions have been obtained for the $^3B_2$ and $^1B_2$ states, which arise from electron configuration (5). For the orthogonal geometry (3), an SCF wave function was obtained for the $^3B_2$ ground state arising from configuration (13). The computations were carried using the SCF methods of Hunt, Hay, and Goddard.[20]

A contracted gaussian basis set of double zeta quality was used. For carbon, Huzinaga's (9s 5p) basis[21] was contracted to (4s 2p) following Dunning.[22] A comparable (4s/2s) contraction was adopted for hydrogen, with each gaussian exponent α multiplied by $(1.2)^2 = 1.44$.

The geometries chosen were based on a C-C distance of 1.43 Å, and a C-H distance of 1.10 Å. The C-C-C and H-C-H angles were taken to be 120°.

RESULTS AND DISCUSSION

The SCF energy for the $^3A_2'$ ground state was -154.8252 hartrees. An identical energy was obtained when the same state was described as $^3B_2$. For the $^1E'$ state the restricted SCF energy was -154.7159 hartrees. However, in this case, as expected,[18] the C_{2v} symmetry calculation gave a significantly lower energy. The $^1B_2$ energy was -154.7914 hartrees, or a full 0.0755 hartrees = 47 kcal/mole lower than the result obtained constraining the molecular orbitals to have full D_{3h} symmetry.

The ambiguity of the $^1E'$ energy creates something of a dilemma for the prediction of the $^3A_2' - {}^1E'$ energy separation. The symmetry and equivalence restriction do not affect the $^3A_2'$ energy, but have a profound effect on the $^1E'$ energy. Our contention is that the calculated $^1E'$ energy is artifically high due to the symmetry and equivalence restrictions, and that either the $^1B_2$ or $^1A_1$ energy should be used to obtain the separation. Hence we predict the $^3A_2' - {}^1E'$ separation to be 0.0338 hartrees or 21 kcal/mole. The MINDO/2 calculations of Dewar and Wasson[14] predict this energy difference to be $\sim$ 35 kcal/mole.

The planar $^1A_1'$ state was also studied, with configuration (4) yielding an SCF energy of -154.6200 hartrees. The same state was also studied with no constraints being put on the spatial form of the molecular orbitals. That is, there were 14 doubly-occupied a orbitals and 2 singly occupied a orbitals in this two-determinant wave function.

Interestingly enough, the SCF energy was the same as that obtained with the full D_{3h} symmetry. Actually, this result is predicted by Manne's analysis,[18] since the $^1A_1'$ representation is totally symmetric. Thus we predict the $^1A_1'$ state, which was not studied by Dewar and Wasson, to lie 0.2052 hartrees or 128 kcal/mole above the ground state. However, the correlation energy of the $^1A_1'$ state should be significantly greater[23] (perhaps 10 kcal/mole) than that of the $^3A_2'$ state, and thus a somewhat smaller separation is expected.

For the orthogonal geometry (3), the $^3B_1$ ground state energy, corresponding to electron configuration (13), was -154.7982. Thus the twisted molecule is predicted to lie 17 kcal/mole above the planar geometry. In a valence bond picture, of course, this preference for planarity can be rationalized in terms of a loss of "resonance" energy at the orthogonal geometry. Due to the ambiguity in correlating the two lowest orthogonal singlets with the planar $^1E'$ state, and the resulting difficulty encountered by Dewar and Wasson in their semi-empirical study, it was decided not to attempt to follow the

$$^1E' \rightarrow {}^1B_1$$
$$^1E' \rightarrow {}^1A_1$$

paths for the twisting of trimethylenemethane. However, a single SCF calculation was carried out for the open-shell singlet, $^1B_1$ state, at the orthogonal geometry. The energy obtained was -154.7958

hartrees, only 1.5 kcal/mole above the $^3B_1$ ground state energy at this geometry. This same separation appears to be $\sim$ 3 kcal/mole in the calculations of Dewar and Wasson.[14] Finally, we predict the orthogonal geometry of the open shell singlet to lie 4.3 kcal/mole below the planar $^1B_2$ component of the $^1E'$ state.

The electronic structure of the triplet ground state may be discussed further in terms of the orbital energies and Mulliken populations, given in Table I (planar geometry) and in Table II (orthogonal geometry). Perhaps the first point to be made is that the σ and π orbital energies are well separated. For the planar geometry, Table I shows the highest σ orbital (4e') to have $\varepsilon = -0.5236$ hartrees, whereas the lowest π orbital ($1a_2''$) has $\varepsilon = -0.4383$ hartrees. Thus it may be reasonable to discuss the excited states of $C(CH_2)_3$ without reference to the σ orbitals.

The correspondence between the orbitals of planar and orthogonal trimethylenemethane is greatly simplified by comparison of the orbital energies. The planar $1a_1'$ orbital is a 1s orbital on the central carbon and is essentially identical to the orthogonal $1a_1$ orbital. The nearly degenerate 1e' and $2a_1'$ orbitals correlate with the $1b_2$, $2a_1$, and $3a_1$ orbitals. These are 1s orbitals on the terminal carbon atoms. Note that for the orthogonal geometry, the orbital ($3a_1$) corresponding to the twisted methylene group has a noticeably higher orbital energy. The $3a_1'$ and $4a_1$ orbitals have very close ε's and similar composition, a symmetric combination of carbon 2s orbitals, with a central carbon contribution of $\sim$ 43%. The 2e' orbital decomposes into the $5a_1$ and $2b_2$ orbitals upon

twisting. These orbitals are primarily terminal carbon 2s in nature, with a significant contribution (∿ 18 %) from hydrogen 1s. The $4a_1'$ orbital becomes $6a_1$ upon twisting and is a conglomeration of all the atomic orbitals except the central carbon p functions. The 3e' orbital is clearly related to the $7a_1$ orbital; they have nearly identical orbital energies and have their greatest contribution from the outer carbon p orbitals, with, in addition, ∿ 27 % hydrogen 1s character.

For the orthogonal geometry, the orbital energies of $3b_2$ and $1b_1$ differ by only 0.003 hartrees and hence it is not immediately obvious which of these correlates with the second component of the planar 3e' orbital. In this regard, note also that the next planar orbital, the $1a_2'$, has no obvious counterpart among the orthogonal orbitals. We conclude that, as a pair, the b component of the 3e' orbital and the $1a_2'$ orbital correlate with the ($3b_2$, $1b_1$) pair, but that some mixing of orbitals occurs during the twisting motion. The 4e' orbitals decomposes into $4b_2$ and $8a_1$ upon twisting and is a combination of carbon 2p and hydrogen 1s functions.

With the exception of the 1e'' orbital, the orbital energies for the excited $^1E'$ and $^1A_1'$ states are within 0.02 hartrees of those for the $^3A_2'$ ground state. For the $^3A_2'$, $^1E'$, and $^1A_1'$ states, the 1e'' orbital energies are, respectively, -0.3211, -0.2088, and, -0.1142 hartrees. This result is by no means unreasonable, since the positive ion for all three of the electronic states is the same $^2E'$ state. Further, the differences

in orbital energies are quite similar to the total energy differences.

In light of the history behind trimethylenemethane, the π orbitals are of greatest interest. We have already noted that the π orbital energies are significantly higher than those of the fourteen σ orbitals. In the case of D_{3h} symmetry, the $1a_2''$ and $1e''$ orbitals are restricted to be composed only of π functions, 2p functions pointing out of the plane of the molecule. Thus the $1a_2''$ orbital is $\sim$ 50 % central carbon $2p\pi$, with a $\sim$ 17 % contribution from each terminal $2p\pi$. This orbital is depicted in Figure 1, a perspective plot of the orbital in a plane 0.7 bohrs above the plane of the molecule. In going to the orthogonal geometry, $1a_2''$ becomes a $2b_1$ orbital. The b_1 irreducible representation is not strictly limited to $2p\pi$ functions. In fact there is a finite contribution to the $2b_1$ orbital from s and p functions on each of the four carbons and from all but the orthogonal hydrogen s functions. The latter atomic functions are of a_1 irreducible representation. Nevertheless, the $2b_1$ orbital remains primarily π-like in character, being $\sim$ 43 % central carbon $2p\pi$, with $\sim$ 24 % $2p\pi$ contribution coming from each of the two methylene groups remaining in the plane of the D_{3h} molecule. These characteristics are seen qualitatively in Figure 2, a perspective plot analogous to Figure 1. Comparison of Figures 1 and 2 shows that in going to the orthogonal geometry the contribution of the twisted methylene carbon essentially disappears, with contributions from the other three $2p\pi$ orbitals becoming appropriately larger. Thus it is easy to imagine the $1a_2''$ orbital

growing[24] into the $2b_1$ orbital in a smooth and continuous manner. In addition, the absence of a significant contribution of the orthogonal methylene carbon to the $2b_1$ orbital may be associated with the loss of resonance energy, which causes the twisted form to lie $\sim$ 17 kcal/mole above the planar molecule.

The singly-occupied orbitals follow our qualitative discussion of the previous section. That is, Figure 3 and 4 demonstrate the essential correctness of our qualitative picture (11). As suggested earlier, the detailed calculations show the $1e_y''$ orbital to become the $1a_2$ orbital as the methylene group is twisted. In fact, a perspective plot of the $1a_2$ orbital is virtually indistinguishable from Figure 4, the $1e_y''$ orbital. We have not plotted the $5b_2$ orbital, since it has little magnitude in the plane 0.7 bohrs above the molecule. However, inspection of the expansion coefficients show the $5b_2$ orbital to be as in (12), a 2p orbital in the plane of the four carbon atoms. Finally, the total π electron density for the $^3A_2'$ ground state is seen in Figure 5.

To conclude, we note the total atomic populations in Tables I and II. In both the planar and twisted configurations, the central carbon has a large positive charge, if discussions of atomic charges are meaningful. In fact, the charge of +0.62 on the planar central carbon is one of the largest we have encountered on any carbon atom study by <u>ab initio</u> methods with comparable basis sets. In hydrocarbons, the carbon atoms usually have populations greater than 6.0, while for CF_2 and C_2F_4 the carbon charges obtained[25,26] are 0.36 and 0.53. The only positive charges larger than +0.62 with

which we are familiar are those obtained by Snyder and Basch for CHF_3 (+0.67) and CF_4 (0.96). Thus it is quite conceivable that as well as having the lowest possible free valence,[1] the central carbon in trimethylenemethane may have the greatest "atomic charge" attainable in a hydrocarbon molecule.

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Table I. Orbital energies and Mulliken populations for the triplet ground state of planar trimethylenemethane. The totals take into account the equivalence of the terminal carbon atoms and of the hydrogens.

		Central C		Terminal C		Hydrogen
Orbital	ε (hartrees)	s	p	s	p	s
$1a_1'$	-11.2690	2.00	0.00	0.00	0.00	0.00
1e'	-11.2447	0.00	0.00	4.00	0.00	0.00
$2a_1'$	-11.2446	0.00	0.00	2.00	0.00	0.00
$3a_1'$	-1.0956	0.84	0.00	0.96	0.13	0.08
2e'	-0.9082	0.00	0.09	3.00	0.09	0.72
$4a_1'$	-0.7189	0.29	0.00	0.35	0.71	0.65
3e'	-0.6327	0.00	0.41	0.05	2.35	1.19
$1a_2'$	-0.5437	0.00	0.00	0.00	1.03	0.97
4e'	-0.5236	0.00	0.77	-0.01	1.99	1.25
$1a_2''$	-0.4383	0.00	0.99	0.00	1.01	0.00
1e''	-0.3211	0.00	0.00	0.00	2.00	0.00
TOTALS		3.12	2.26	3.45	3.13	0.81
ATOM TOTALS		5.38		6.58		0.81

Table II. Orbital energies and Mulliken populations for triplet trimethylenemethane in its orthogonal configuration (3).

		Central C		Terminal C		Orthogonal C		Hydrogen a	Hydrogen b	Orthogonal Hydrogen
Orbital	ε (hartrees)	s	p	s	p	s	p	s	s	s
$1a_1$	-11.2697	2.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$1b_2$	-11.2467	0.00	0.00	2.00	0.00	0.00	0.00	0.00	0.00	0.00
$2a_1$	-11.2467	0.00	0.00	2.00	0.00	0.00	0.00	0.00	0.00	0.00
$3a_1$	-11.2335	0.00	0.00	0.00	0.00	2.00	0.00	0.00	0.00	0.00
$4a_1$	-1.0944	0.86	0.00	0.66	0.08	0.30	0.04	0.01	0.03	0.02
$5a_1$	-0.9081	0.00	0.08	0.49	0.07	0.97	-0.01	0.08	0.05	0.27
$2b_2$	-0.9049	0.00	0.13	1.45	0.03	0.00	0.02	0.19	0.19	0.00
$6a_1$	-0.7158	0.28	0.00	0.24	0.47	0.13	0.45	0.21	0.21	0.21
$7a_1$	-0.6334	0.00	0.20	0.01	0.95	0.01	0.25	0.07	0.39	0.11
$3b_2$	-0.6002	0.00	0.36	0.01	1.08	0.00	0.04	0.52	0.00	0.00

Table II Continued

Orbital	ε (hartrees)	Central C		Terminal C		Orthogonal C		Hydrogen a	Hydrogen b	Orthogonal Hydrogen
		s	p	s	p	s	p	s	s	s
$1b_1$	-0.5972	0.00	0.15	0.00	0.05	0.00	1.05	0.00	0.00	0.76
$4b_2$	-0.5297	0.00	0.25	0.00	1.00	0.00	0.00	0.10	0.64	0.00
$8a_1$	-0.5204	0.00	0.37	0.00	0.56	0.00	0.45	0.42	0.09	0.11
$2b_1$	-0.3867	0.00	0.87	0.00	0.97	0.00	0.05	0.00	0.00	0.13
$5b_2$	-0.3750	0.00	0.01	0.00	0.00	0.00	0.98	0.01	0.00	0.00
$1a_2$	-0.2895	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00
TOTALS		3.14	2.41	3.42	3.14	3.40	3.08	0.808	0.806	0.805
ATOM TOTALS		5.55		6.56		6.48		0.808	0.806	0.805

FIGURE CAPTIONS

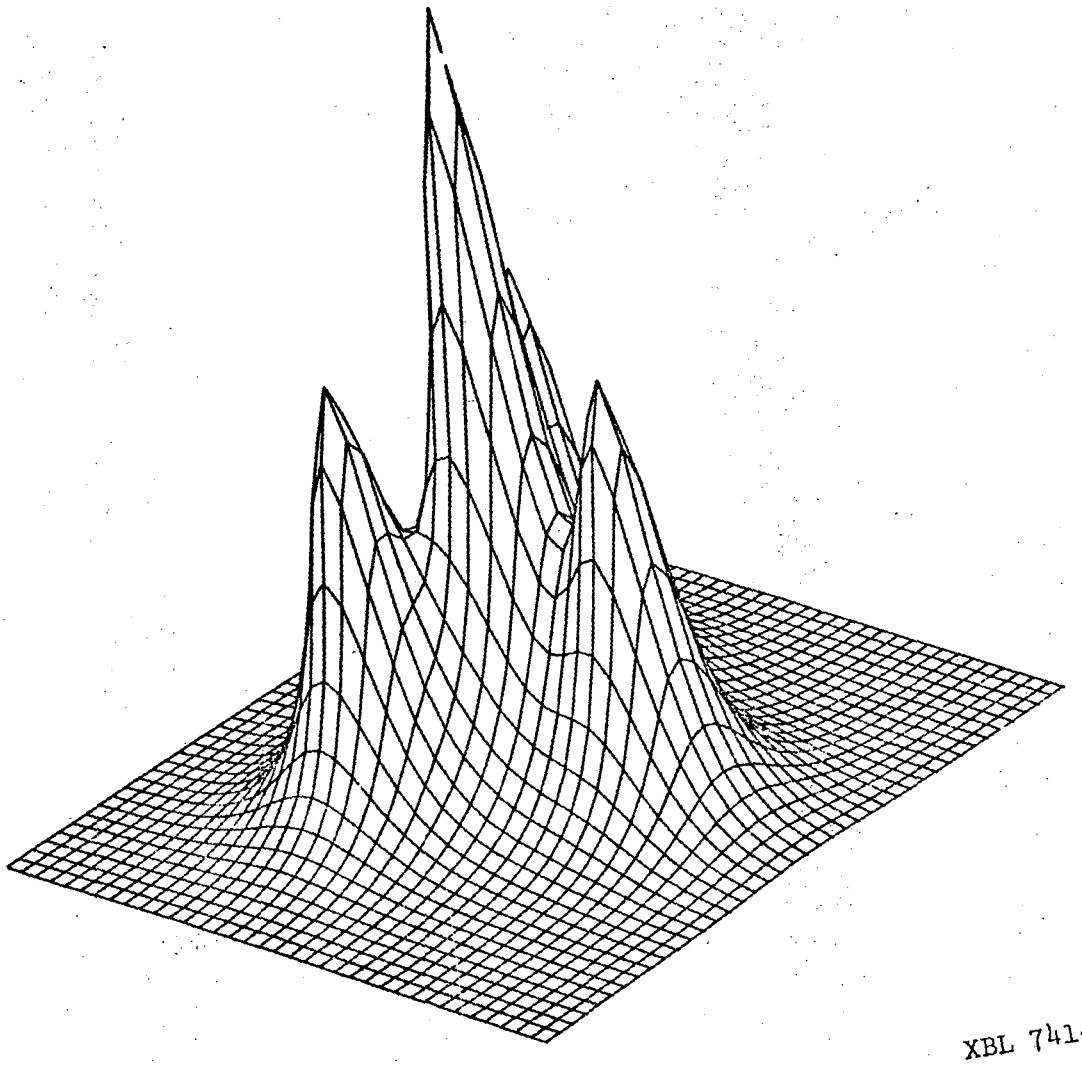
Figure 1. Perspective plot of the $1a_2''$ orbital of planar triplet trimethylenemethane in a plane 0.7 bohrs above the molecular plane.

Figure 2. Perspective plot of the $2b_1$ orbital of twisted triplet trimethylenemethane.

Figure 3. The $1e_x''$ orbital of $C(CH_2)_3$.

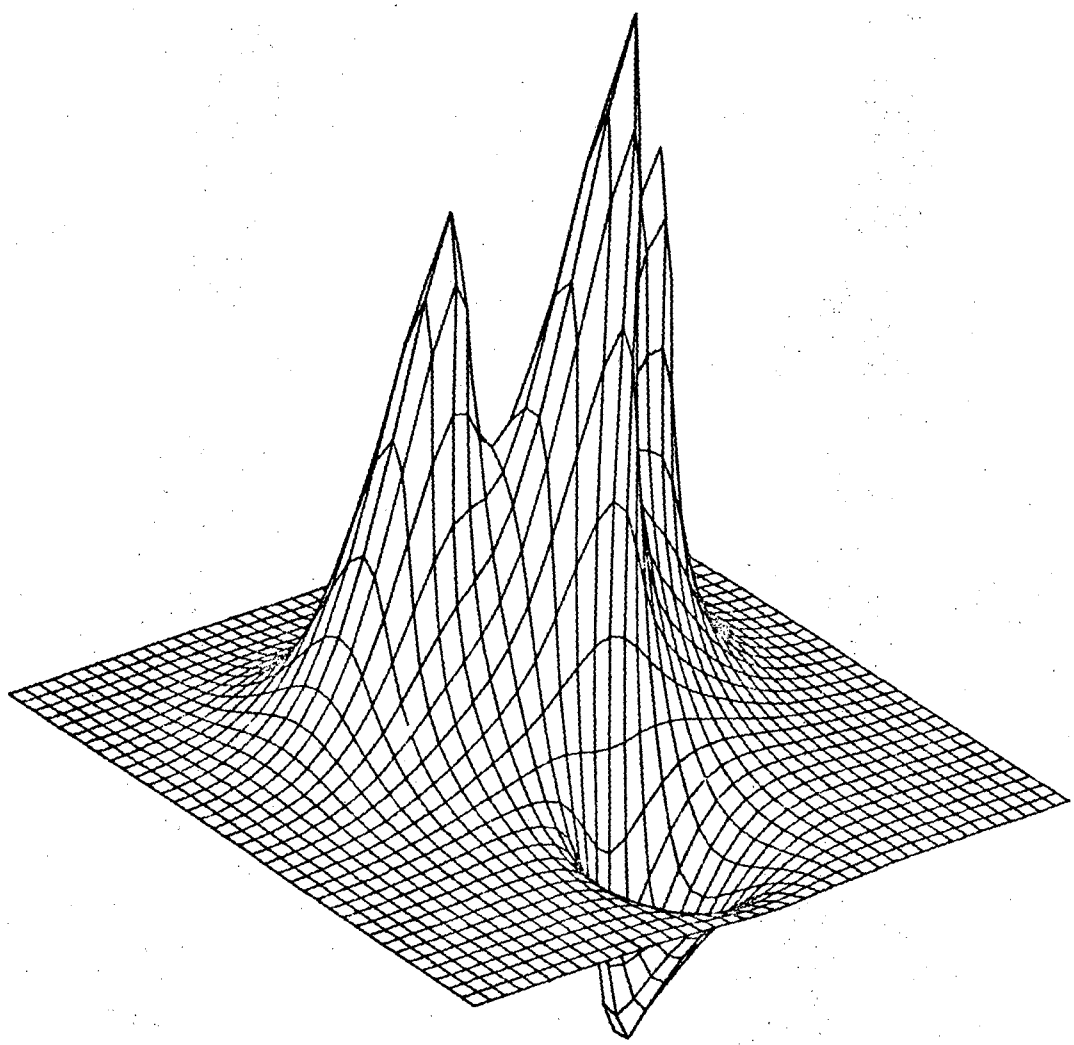
Figure 4. The $1e_y''$ orbital of $C(CH_2)_3$.

Figure 5. Total π electron density of trimethylenemethane in a plane 0.7 bohrs above the molecular plane.



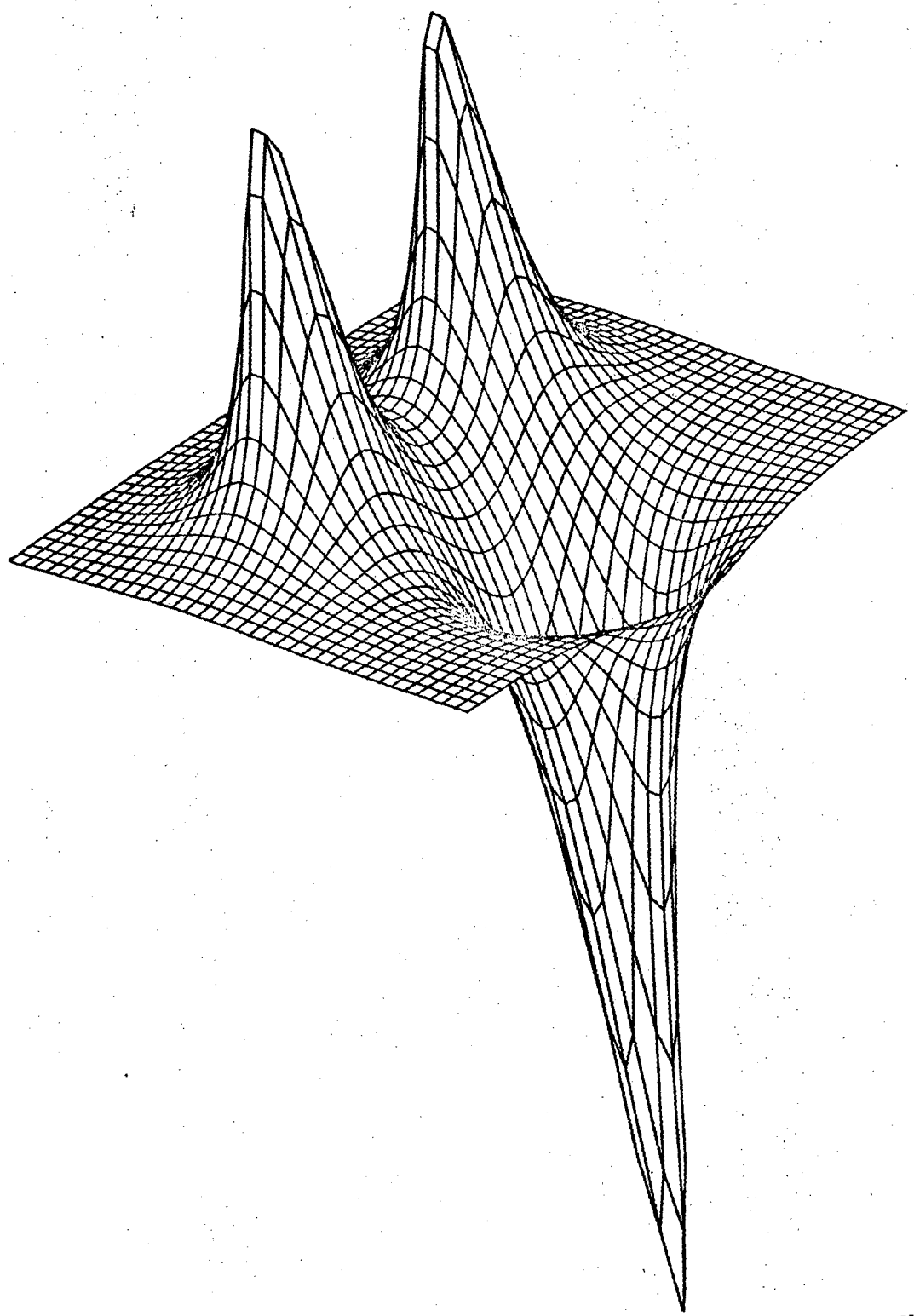
XBL 741-3

Fig. 1



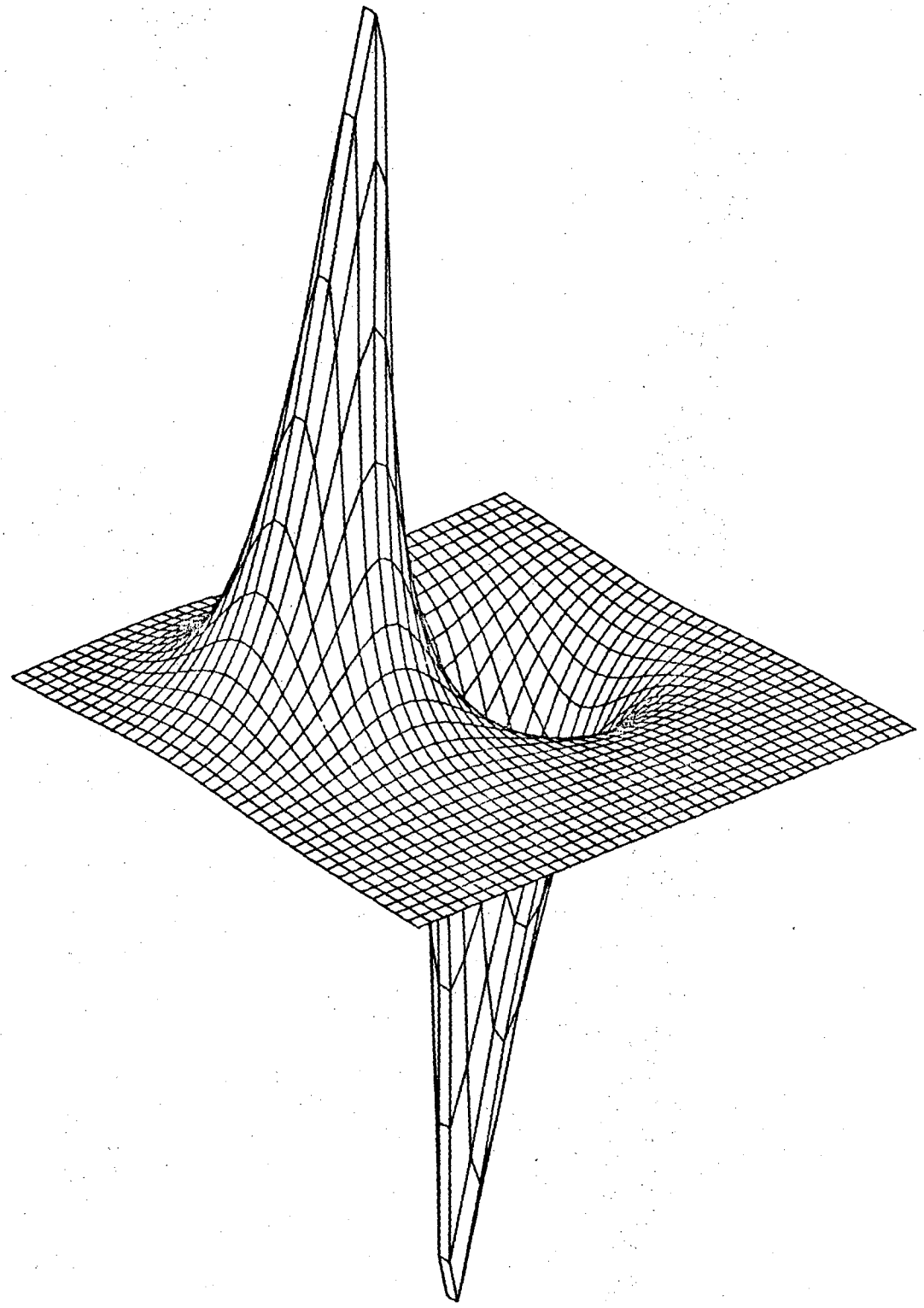
XBL 741-4

Fig. 2



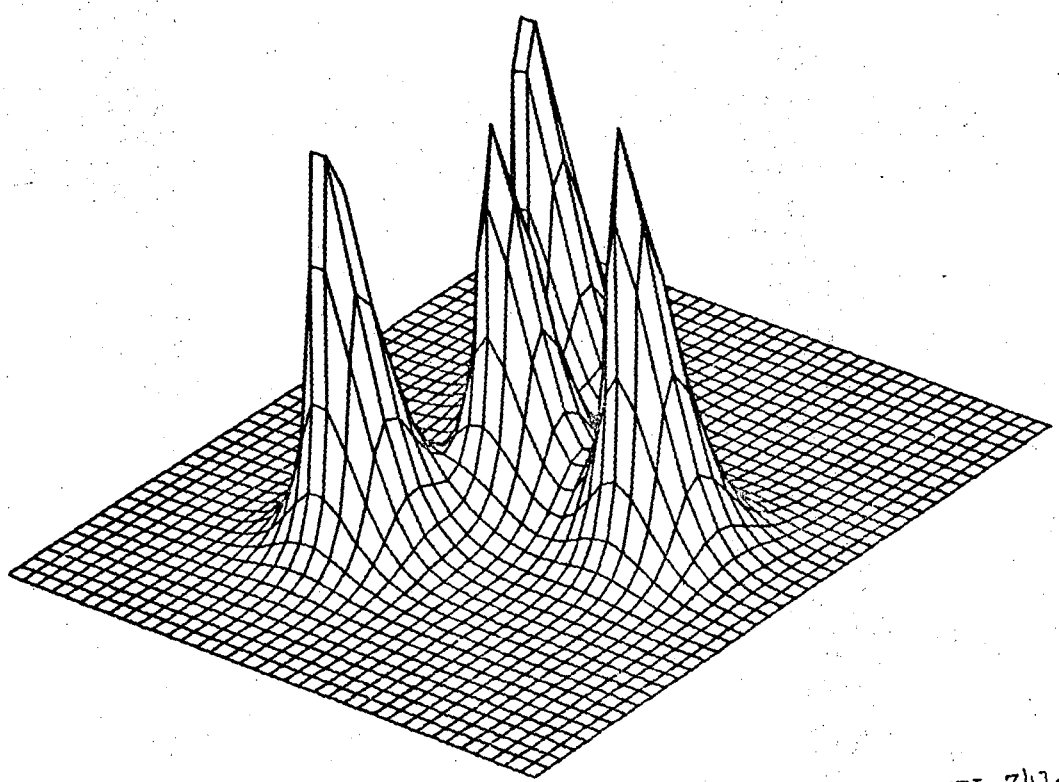
XBL 741-1

Fig. 3



XBL 741-2

Fig. 4



XBL 741-5

Fig. 5

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