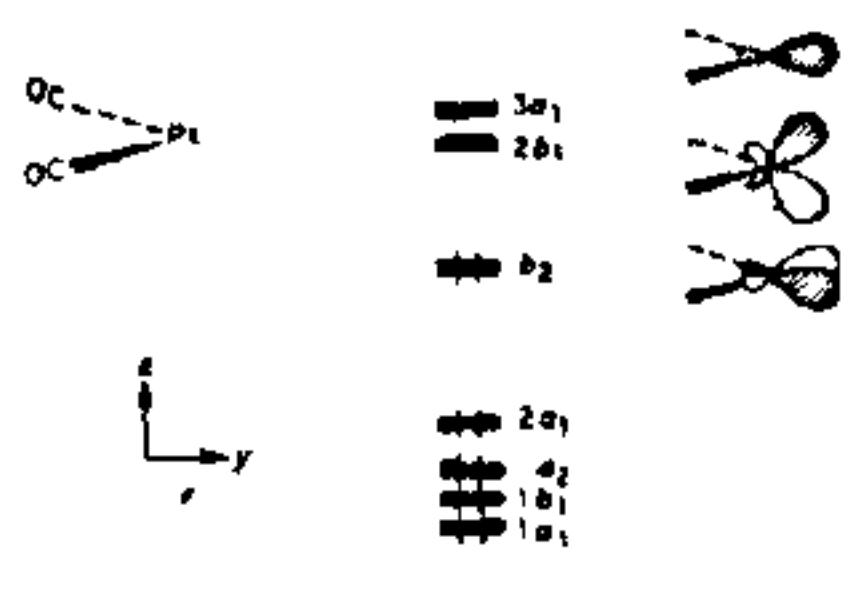


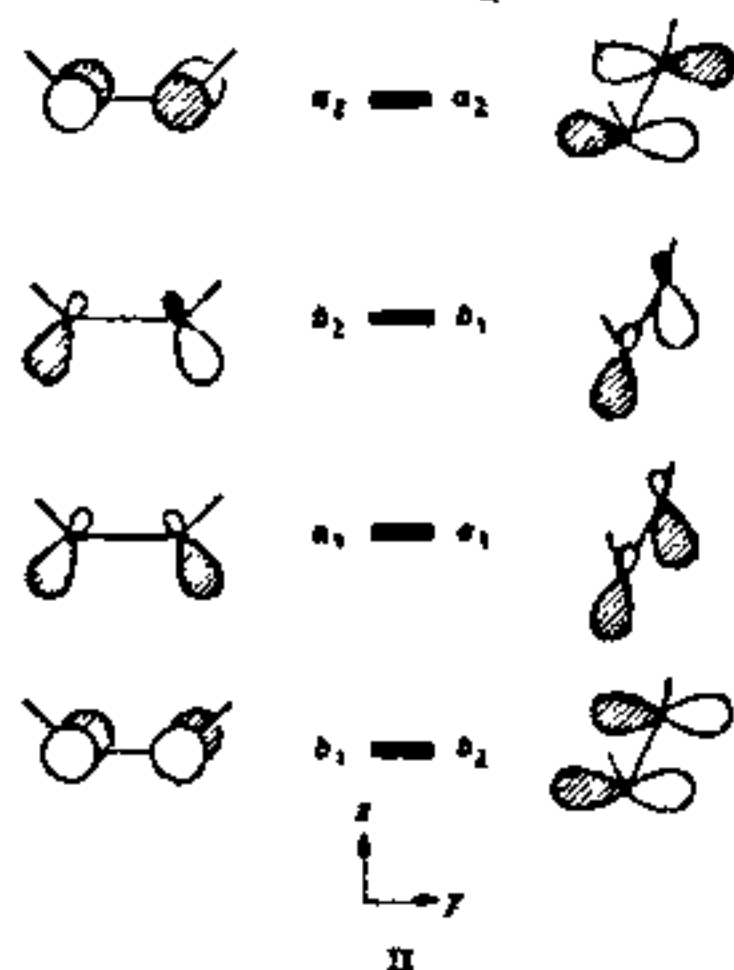


matically in I. A detailed discussion of the  $ML_4$   $m o s$  has been given before.<sup>6</sup> At low energy is a block of four  $d$  orbitals which are related to the similar block characteristic of a square-planar complex  $ML_4$ . Such an  $ML_4$  complex can be thought of as a parent to  $ML_5$ , and the two orbitals of primary concern to us,  $3d_x$  and  $3d_y$ , can be viewed as in- and out-of-phase combinations of hybrids

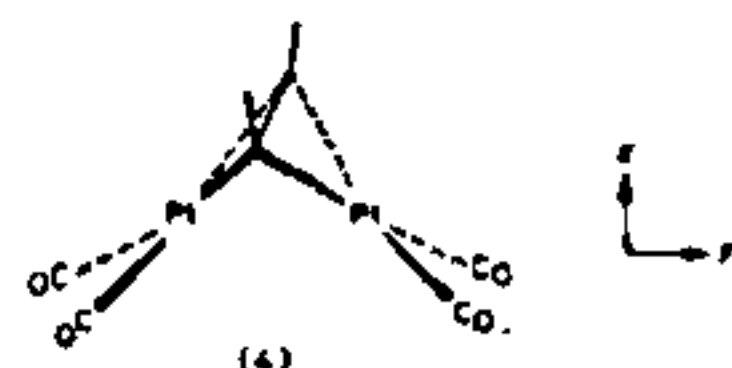


left behind by removing two ligands from  $ML_4$ . Orbital  $b_2$  is a  $pd$  hybrid ( $px + xz$ ) with lobes protruding toward the vacant  $ML_4$  sites. Orbital  $3a_1$  is mainly a metal  $sp$  hybrid with some  $d$ -orbital character. The  $b_1$  orbital that lies in energy between  $b_2$  and  $3a_1$  is concentrated on the CO ligands and will not be of importance until later in our analysis.

Co-ordinated acetylenes, whether perpendicular or parallel are invariably cis bent at the carbons. We prepare an acetylene for bonding in our complexes by taking an HCC angle of  $130^\circ$ . The resulting orbital pattern is shown in II. Bending breaks the  $ac \pi$  and



$\pi^*$  degeneracies, with some consequent rehybridization of one acetylene  $\pi$  system. When we examine parallel and perpendicular alternatives we will opt for the (arbitrary) choice of rotating the acetylene rather than the  $L_4ML_4$  framework. For this reason some of the acetylene orbitals change symmetry designation



In Figure I is given an interaction diagram for a  $(CO)_2PtPt(CO)_2$  fragment with neutral cis bent ac to give (4). The orbital pattern on the left for  $(CO)_2PtPt(CO)_2$  consists of essentially the in-phase and out-of-phase combinations of the orbitals in I brought together in the geometry appropriate to (4). The lower eight-orbital

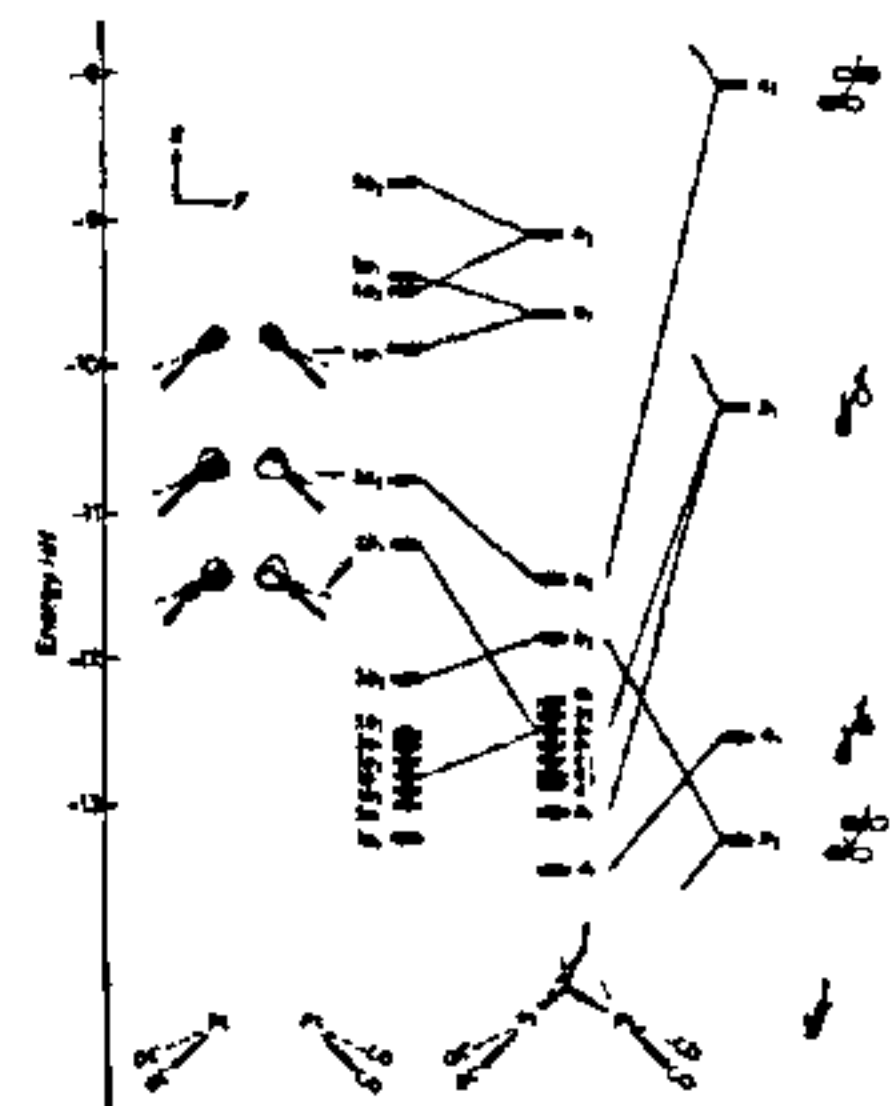


FIGURE 1. The interaction of  $(CO)_2PtPt(CO)_2$  with  $C_2H_2$  in the perpendicular geometry. The Pt-Pt distance is 2.82 Å.

block is derived from  $1a_1$  through  $2a_1$  in I and the upper filled  $m o s$ ,  $2b_1$  and  $2a_2$ , come from  $b_2$ . The empty orbitals above  $2a_2$  are combinations of  $2b_1$  and  $3a_1$  of  $Pt(CO)_2$ . In the perpendicular orientation the  $ac$  donor orbitals transform as  $a_1$  and  $b_2$ , see II. They interact with the

Figure 3.

two in  $\pi^*$ , so that an Fe=O double-bond notation is appropriate.

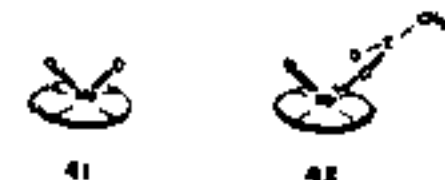
We have employed  $H_2O$  as an axial ligand in order to compare the electronic structure of oxo-iron porphyrin with that of carbene-iron porphyrin (Figure 5) later in this section. The axial position in the biologically important oxoporphyrin is likely to be occupied by a base such as imidazole. However the difference in electronic properties between  $H_2O$  and nitrogenous bases is not significant, in the sense that both act as weak  $\pi$  donors in an axial coordination site of porphyrin complexes.

Another possible structure of oxo-iron porphyrins is a square pyramid which has no additional axial ligand, as shown in (6).



Removal of an axial  $\pi$  donor from a pseudooctahedral geometry should stabilize the  $x^2(4e_g)$  orbital. This trend was confirmed by a calculation on  $O=Fe$ -porphyrin: the Fe moved out of the porphyrin plane by 0.5 Å. The basic pattern of the interaction diagram of Figure 7 is carried over to  $O=Fe$ -porphyrin, except that the  $x^2(3a_1)$  level is now at -9.4 eV (instead of being at -6.5 eV).

It is easy to understand why ferryl complexes are so unstable. Two electrons are in the  $xz(1b_1)$  and  $yz(1b_2)$  levels. These are antibonding combinations of  $Fe d_x$  and  $O p_y$  orbitals. Thus the Fe=O  $\pi$  bond is substantially weakened. If two or more electrons are removed from the ferryl system, one can get more stable oxometalporphyrin complexes. Examples of  $d^0$  ( $n < 4$ ) molecules are many:  $(O=M-OEP)(X)$  ( $M = Nb, X = F, d^0$ ;  $M = Mo, X = OMe, d^0$ ;  $M = W, X = OPh, d^0$ ;  $M = Re, X = OPh, d^1$ );  $(O=M-OEP)_2O$  ( $M = Nb, d^0-d^2$ ;  $M = Mo$  and  $W, d^1-d^3$ ;  $M = Re, d^2-d^3$ );  $O=V$ -porphyrin ( $d^1$ ); porphyrin = etioporphyrin, mesoporphyrin IX, dimethyl ester, deuteroporphyrin IX, dimethyl ester, and TPP<sup>90</sup>;  $O=M$ -tetramethylammoniumchlorate ( $M = Cr$  and  $Mo, d^1$ );  $O=Re$ -octaethylcorrole ( $d^1$ );  $O=Ti$ -tetra-*tert*-butylporphyrin ( $d^0$ );  $(O=Cr-TPP)(Cl)$  ( $d^1$ ); and  $(O=Mo-TPP)(Cl)$  ( $d^1$ ).<sup>91</sup> Among these, X-ray diffraction analyses are available for  $(O=Mo-TPP)_2O$ ,<sup>92</sup>  $O=V$ -deoxyphytylerythrotoporphyrin, and  $(O=Mo-TPP)Cl$ .<sup>93</sup> Oxometalporphyrins sometimes have an extra ligand which sits cis to the oxygen atom, on the same side of the porphyrin plane, e.g.  $MoO_2(TPP)_2$ <sup>94</sup> (41) and  $(O=Nb-TPP)(OOCCH_2)(CH_2COOH)$ <sup>95</sup> (42).



Recently Loew and Herman calculated by an INDO method

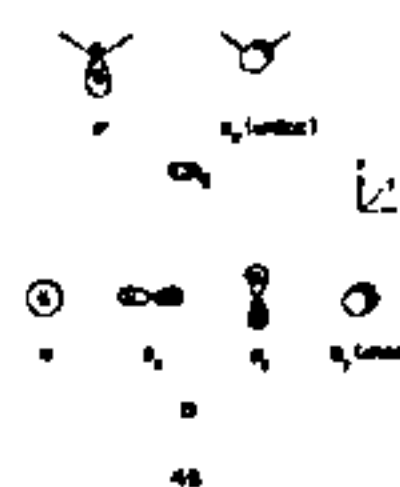
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- (46) Lodon, H.; Bollen, M. *J. Chem. Soc. Chem. Commun.* 1979, 102-104; Metzger, B.; Bollen, M.; Lodon, H. *J. Inorg. Chem.* 1980, 19, 2061-2066.

used the spin density distribution in porphyrin-ferryl complexes which are models for intermediates in the enzymatic reaction of horseradish peroxidase HRP I and HRP II.<sup>96</sup> Our ferryl model of structure 39 is very close to the HRP II model ( $S = 1$ ). The calculated unpaired electron densities for 39 (in an open shell configuration appropriate to  $S = 1$ ) are illustrated in (43). Most of the unpaired electrons reside on the



central Fe atom and some of them are distributed to the oxo ligand. Electron densities on atoms in the porphyrin ring are very small. These trends obtained here by extended Hückel calculations accord with the results of INDO calculations for the HRP II model.<sup>96</sup> The unpaired electron density distribution in the molecule 40 (again in an  $(xz)^2(yz)^1$  configuration) is given in (44). The out-of-plane displacement of the Fe=O group and the removal of an axial ligand increase the spin densities on the porphyrin ring, but only slightly.

It is interesting to compare the electronic structures of oxoiron porphyrins and those of carbeneiron porphyrins. If we think of an oxygen atom as neutral and put six valence electrons in  $2s$  and two  $2p$  orbitals, leaving  $2p$ , vacant, (45), then



that configuration of oxygen and that of carbene are iso-electronic. Indeed the carbene-oxygen analogy has figured prominently in discussions of biological oxygenation systems.<sup>97</sup> The similarities of O and  $CH_2$  in their bonding to an iron porphyrin are apparent from Figures 5 and 7.

One major difference between O and  $CH_2$  is that O has two  $p_z$  orbitals which interact with  $Fe d_x$  orbitals while  $CH_2$  has only one. The last two electrons of  $d^0$  ( $O=Fe$ -porphyrin)( $H_2O$ ) enter the  $Fe d_x - O p_z$   $\pi^*$  levels. In contrast the  $Fe d_x - C p_z$   $\pi^*$  orbital of  $d^0$  ( $Fe$ -porphyrin)( $CH_2$ )( $H_2O$ ) is unoccupied. Thus it is a carbene complex with two more electrons in the  $\pi^*$  orbital, i.e. a  $d^2$  carbene-nucleated porphyrin of the structure 25 or 36, which is analogous to  $d^2$  ( $O=Fe$ -porphyrin). Both molecules should be and are, relatively unstable.

The other difference between O and  $CH_2$  is their  $p$  ( $or \pi$ ) orbital energies. The O  $p$  energy is much lower than the Fe  $d$  energy while  $CH_2$   $p$  lies very close to Fe  $d$ . Thus the  $d_x, p_z$  ( $and \pi^*$ ) orbital of  $O=Fe$  are more polarized than those of  $H_2C=Fe$ . The  $\pi^*$  orbitals of  $H_2C=Fe$  and  $O=Fe$  in

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Figure 4.

of the final paper, I've pasted in xerox copies of a piece of my collaborator's draft that I decided to include in the final draft.

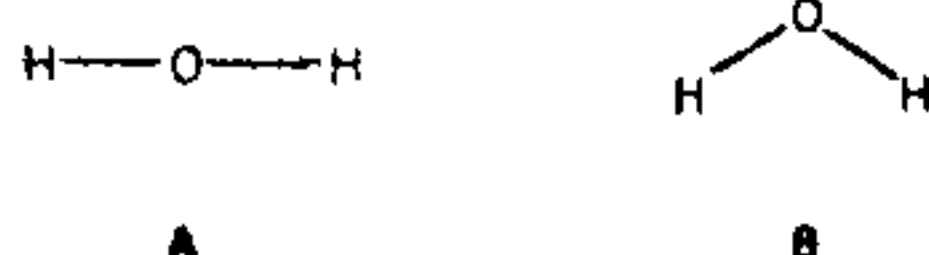
The actual drawings that the scientific journals print are reproduced from India-ink originals on tracing paper. These are masterfully done by Jane Jorgensen and Elisabeth Fields, two illustrators who have worked with me many years. They trace the ink drawings from carefully designed pencil sketches made by me or my coworkers.

Are these art, these collage-like manuscript pages and the final product? They look like science. But what I would like to claim is that there is much more art in these assemblages of symbols than the scientist would admit or the artist allow.

Let us focus first on the most obvious visual feature of my printed scientific article, and this is the preponderance of little drawings of molecules. These are 'chemical structures'. They represent, in a visual code, molecules. The representa-

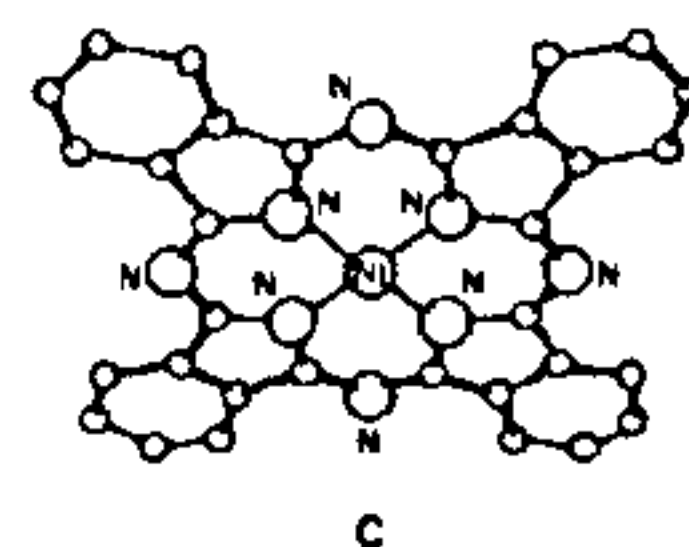
tion is three-dimensional. And it is realistic, at least on the face of it. But is it?

The shape or structure of molecules is critical. Every chemical, physical and biological property depends on the three-dimensional arrangement of atoms in space.<sup>2</sup> If water,  $H_2O$ , were 'linear', A, and not bent (B, as it really is) it probably would not be a liquid at ambient temperatures at the surface of the earth, and life as we have it would not exist. The mirror image of a molecule that is the essence of oil of wintergreen smells like spearmint.



What chemists can obtain, with the help of machines costing many thousands of dollars and a man- or woman-week of work, is the identity of atoms in a molecule, how they are connected to each other ( $H_2O$  and not  $H_3O$ ,  $H-O-H$

and not  $H-H-O$ ), and their three-dimensional structure. That structure is presented usually as a 'ball-and-stick' model, a typical example of which is shown in C. This happens to be a phthalocyanine, representative of an important class of pigments that modern chemistry has added to the palette.



It turns out that this representation is ambiguous. The atoms don't sit still, they vibrate around certain preferred sites. And when we look at them we don't see the nuclei, whose positions C represents, but the electron clouds around them. Chemists know this—the ambiguity of the model—but they will not admit to it unless forced to by an argumentative, perverse insider.<sup>3</sup>

But let us pass by that, and continue. The model of the molecule is three-dimensional. The media available for disseminating its absolutely crucial structure are two-dimensional—a sheet of paper, a screen. And, what's worse, the group of people who need to communicate this information is neither talented nor trained to produce effective two-dimensional representations. Chemists are not sent to drawing classes. So what do they do? They improvise a primitive visual code, combining some elements of mechanical drawing (few, note the poor perspective in the Figures) with a code (a wedged line means 'in front', a dashed line 'in back'). And they indoctrinate novices in the second year of college chemistry, with the aid of models, into that code. It's quite miraculous, that, from these primitive representations floating in some undefined space, chemists can reconstruct in their minds three-dimensional networks of some complexity. Here is testimony to the strength of symbolic codes and the inherent, irrepressible ability to see structures as three-dimensional.

Pierre Laszlo and I have written elsewhere of the symbol code of these structures, and its peculiar relationship to 'primitive' art and the genres of caricature and cartoons<sup>3</sup>. What my colleagues have evolved is a method of representation that selects, for emphasis, some aspects of the model, those that they chose to choose. Then they put it visually up front, that selected feature. If another time they want to represent another aspect of the molecule—no problem, just bring that part of it up front. It is no coincidence that photographs have found little use in chemistry journals (or anatomy books). Not that I want to argue at all that a photograph is a realistic representation. But a photograph has *too much* detail, and *not enough* at the same time, not enough of the essence of the molecule that one chemist is desperately trying to communicate to another.

In the drawings before you, let me draw your attention to the history that is being developed by the crossing out in Figure 2. Kaz Tatsumi and I were faced with the problem of representing a disc-like molecule called a porphyrin, with a molybdenum or niobium at its centre. Porphyrins are close, chemically, to the phthalocyanines mentioned ear-

lier. With iron in the ring they are the active piece of the oxygen carrier, haemoglobin, in our red blood cells. Slightly modified, with a magnesium in the middle, they are chlorophyll. Anyway, we first made the choice of showing all the atoms in the ring (but not the hydrogen at its periphery). Then we decided this was an inadequate (or overly detailed) representation, and opted for a schematic ring with four lines, like spokes, to the metal in the middle. You see direct evidence here of choices being made, of representations altered for expressive purposes. If you look at structures 43 and 44 in Figure 4 you will see a different choice of representation for the porphyrin ring than in 40, 41, 42. There was a reason for this back-and-forth.

My claim is that these chemical structures are art. Not great art, but art nevertheless. Even if their creators are unaware that they are producing art, even if they would deny the act—the conceit (many scientists would say, revealing thereby an interesting ambiguity toward art)—of being artists, what they are doing is the following: From a certain reality (which, as all realities, on close examination turns out to be a representation of a representation of . . .), that of a molecular model, they try, as hard as they can, to abstract the essence. Then they attempt to communicate that essence, using a certain visual vocabulary, to others. There is a concentration in what they do, an intensity that makes the object marked for communication come to life. There is also a distancing from the object (it's drawn from outside, remote) and a drawing in. Significant formal considerations, the relationship of the parts of a molecule to its whole, are essential.

An argument can be made that what is missing is (a) the chanced, therefore unique, aspect of artistic creation, and (b) the affective realm, the play of the emotions in this process of communication. To expand on the first point, which I think has some merit: while an artist's *oeuvre* reveals similarities, each work is different, a varied creation. The aleatory aspect, capitalized upon, is central. Scientific representations aspire, on the other hand, if not to anonymity, then to perfect paraphrase<sup>4</sup>. All those chemists who wind up drawing slightly different structures want other chemists to see the same molecule. And they do.

I will not argue too strongly with that. However, it has been my personal experience that despite the announced or perceived intent of perfect paraphrasability, the creative moment in chemistry derives from a perception (often spatial) of a molecule in just one way and not another. One sees that in the work of great synthetic chemists, master makers of molecules. The model turned in their hand in just one way, a redrawing of a structure with a certain unrealistic distortion allowed them, and only them, to see the molecule in a certain way, to take it apart on the way to finding a startling way to put it together.

As for the emotional realm—well, I would agree that it is repressed in the prescribed discourse of scientists. But first of all, to those privy to the code, that little free-floating picture can have tremendous emotional impact—something novel, something beautiful, a challenge to make, envy of the man or woman who made it. As Nelson Goodman has argued:

... the difference between art and science is not that between feeling and fact, intuition and inference, delight and deliberation, synthesis and analysis, sensation and cerebration, concreteness and abstraction, passion and action, mediacy and immediacy, or truth and beauty, but rather a difference in domination of certain specific characteristics of symbols<sup>5</sup>.

Second, we have learned from literature and Freud what the consequences of suppression are. Here is a creative activity of human beings—science. Deep down it is driven by the same complex mix of psychic motives that drive any creation. The id will out. But the people who are doing it claim to be just reporting the facts and nothing but the facts. At best they may be fooling themselves; the very same impersonal, neutered language in which they choose to express themselves becomes charged with rhetorical impulses, claims to power, all the things they (we) foolishly thought we could suppress<sup>6</sup>.

Perhaps my argument here is over-extended, for the emotional effect of the chemical representation is less obvious in the structures than it is in the *language* of the chemical article. And the printed pages shown in Figures 3 and 4 do not appear to be spontaneous creations.

It could be that the manuscript pages, Figures 1 and 2, fit the art model better.

Their collage-like aspect certainly testifies to planning, to construction. But these word-image constructs have the feel of art—the pencil stroke made here and not there, the words (and pictures) crossed out. My sketch of a molecule is just that, a sketch, but as the David Hockney could draw a 'better beach chair' had he wanted to, I could have drawn a more realistic representation of my molecule. The information in that sketch suffices, at least to me. There is more expressive power in that little drawing than in my final finely drawn product; it bears crude witness to my struggle to understand and explain, to conceptualize and articulate<sup>7</sup>.

There's no chance that any scientific journal would publish that initial sketch.

Or even a 'better one', drawn by a more effective chemical artist. Perhaps this is the impoverishing aspect of this particular mode of human symbol transfer.

#### Notes and references

1. Figure 3 is taken from Hoffman, D. M. and Hoffman, R., *J. Chem. Soc., Dalton Trans.*, 1982, 1471. Figure 4 comes from Tatsumi, K. and Hoffman, R., *Inorg. Chem.*, 1981, 20, 3771.
2. For a good introduction to molecules and their shapes see Atkins, P. W., *Molecules*, Scientific American Library, New York, 1987.
3. Hoffmann, R. and Laszlo, P., *Diogenes*, July–September 1989, No. 147, 24; in slightly different form in *Angew. Chem.*

1991, in press.

4. Stent, Gunther, *Scientific American*, December 1972, 84.
5. Goodman, N., *Languages of Art*, 2nd edition, Hackett, Indianapolis, 1976, p. 264.
6. Some of these points are explored in Hoffmann, R., *Angew. Chem. Engl.*, 1988, 27, 1593.
7. Here I am grateful to Alexis Smith for a clarifying discussion.
8. This material was first published, in slightly different form, in a Cornell Department of Art journal, *Q (A Journal of Art)*, May 1990, p. 62.

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#### National Seminar on Application of Science and Technology in the Conservation of Cultural Property/Heritage (ASTECH)

The seminar, scheduled to be held at IPCL, Baroda, in April, has been postponed.

Contact: Dr (Mrs) S. Amudeswari  
Dept of Science and Technology, GOI  
Technology Bhavan  
New Mehrauli Road  
New Delhi 110 016

#### Sixth Annual Conference of the Ramanujan Mathematical Society

Place: Saurashtra University, Rajkot  
Date: 1–3 June 1991

Focal theme is complex analysis. Ten instructional lectures on moduli of compact Riemann surfaces, other invited talks, seminars on mathematical modelling and operator theory, and paper reading sessions.

Contact: Dr P. B. Ramanujan  
Local Secretary  
Department of Mathematics and Statistics  
Saurashtra University  
Rajkot 360 005

#### Training Course on Plant Tissue/Cell Culture for the Production of Phytochemicals and for Plant Improvement

Place: CFTRI, Mysore  
Date: 8–26 July 1991

For persons from universities, R&D institutions and industries.

Contact: Dr L. V. Venkataraman  
DBJ Course Director  
Area Coordinator  
Central Food Technological Research Institute  
Mysore 570 013  
Phone: 821 22660 Telex: 846 241 FTRI IN

#### Third International Conference on Physiological Fluid Dynamics

Place: Indian Institute of Technology, Madras, India  
Date: 23–26 July 1991

Papers in biorheology, microcirculation, arterial haemodynamics, clinical haemodynamics, red-cell deformability and aggregation, biotransport, atherosclerosis, flow visualization, tissue–drug interaction, high-altitude and deep-sea haemodynamics.

Contact: Dr Megha Singh  
Organizing Secretary, ICPFD  
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Telex: 41 21062 TECHMAS IN  
Fax: (91) 44 412509

#### INCAL-91 International Conference on Aluminium

Place: Bangalore, India  
Date: 31 July–2 August 1991

Subjects include smelter technology, by-product generation and use, pot technology, developments in new alloys, energy savings and new options, structure–property correlations in aluminium-based alloys, aluminium matrix composite materials, surface coating, corrosion, and various fabrication techniques.

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