

Molecular Electronic Devices

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CHAPTER II

MOLECULAR MEMORY AND HYDROGEN BONDING

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INTRODUCTION

Characteristic sizes of electronic components in computer hardware have displayed a relentless shrinkage with the passage of time. While 10 cm might be an appropriate length scale to describe vacuum tube equipment available in 1940, 10 μm spacings on semiconductor chips has become routine in 1980. Each passing decade thus has witnessed reduction in linear dimension by a factor of ten. By obvious extrapolation one concludes that 2020 will be "the year of the nanometer," with computing elements reduced to the size of individual molecules.

Does this kind of extrapolation make sense in useful technological terms? Can single molecules actually serve as reliable computing elements? Intriguing support for affirmative answers to these questions emerges from established fact. Certainly molecular biology demonstrates by concrete example that individual molecules (specifically DNA and RNA) can serve as information storage, replication, and transmittal media. But information processing in the regime of molecular biology is notoriously slow, perhaps having had no evolutionary compulsion to be otherwise. Furthermore it is chemically uncertain that the class of compounds produced and selected by terrestrial chemical evolution could ever become substantially more rapid, efficient, or versatile by conservative structural modifications. Fortunately synthetic chemistry offers a much wider set of opportunities, one aspect of which we explore in this paper. Another approach, based on photochemical hole burning, has been previously explored. (1)

If indeed some part of computer technology is headed for the molecular regime it is time to turn creative intellectual effort in chemistry and physics to the question of how best that can be achieved.

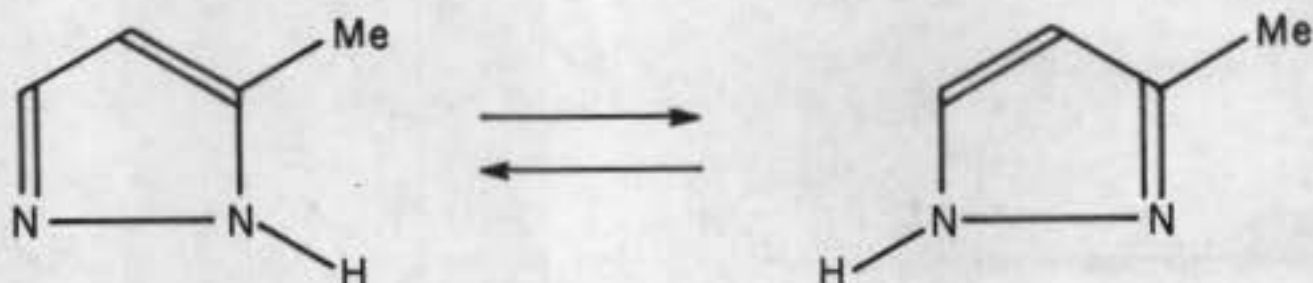
TAUTOMERISM AND SWITCHING

The fact that many molecules can switch between alternative tautomeric forms may provide a phenomenological entree into the desired novel technology. In particular many cases are known involving intramolecular hydrogen atom shifts between alternative binding sites (potential minima). An elementary

example is provided by glycine, the simplest amino acid, as it transforms between undissociated and zwitterionic forms:



5-Methylpyrazole also exhibits a tautomeric hydrogen shift in a manner that obviously couples to the pi electron (double bond) character of the molecular skeleton:



One suspects that switching speeds under appropriate conditions could be extremely fast for protons, perhaps in the subpicosecond range, owing to the small mass of that particle. But protons alone are not interesting in this respect; chemical groups such as methyl or trimethylsilyl could perform with competitive speeds provided that the distance to be traversed were sufficiently small. In any event, for information storage applications it is necessary to have the binding sites inequivalent and separated by a sufficiently high potential barrier so that neither tunneling nor thermal fluctuations can inadvertently switch the molecule from one state to the other. Switching should occur only under external control as by application of a suitable light pulse.

Figure 1 schematically illustrates an ideal situation for photochemical switching. It shows three potential energy curves versus a proton positional coordinate. The lowest curve (a) corresponds to the electronic ground state and exhibits two inequivalent minima labelled "state 0" and "state 1"; these are the tautomeric alternatives. The upper two curves (b,c) are a pair of excited electronic states that afford opportunity for switching. Since the ground state is asymmetric so too will be these upper states.

It is an established experimental fact that electronic excitation can drastically alter shapes of potential energy curves. In particular the relative binding strengths of alternative sites can be reversed, and barriers reduced or eliminated. For the hypothetical example in Figure 1 we have permitted the excited states to show such alteration and to tip respectively right and left.

Optical switching from state 0 to state 1 is initiated by irradiation at frequency $\nu(0 \rightarrow 1)$. This induces a vertical transition to the lower excited-state curve, yielding a vibrationally excited molecule in accord with the Franck-Condon principle. Vibrational relaxation on this upper curve changes the mean value of the proton's x coordinate to conform to that of state 1, roughly. Fluorescence decay then returns the system to the ground-state curve but now with the proton switched. The protonic itinerary is traced out by the sequence of three solid arrows.

The inverse process whereby state 1 is photochemically switched back to state 0 requires the higher excited state, but it is otherwise similar. The

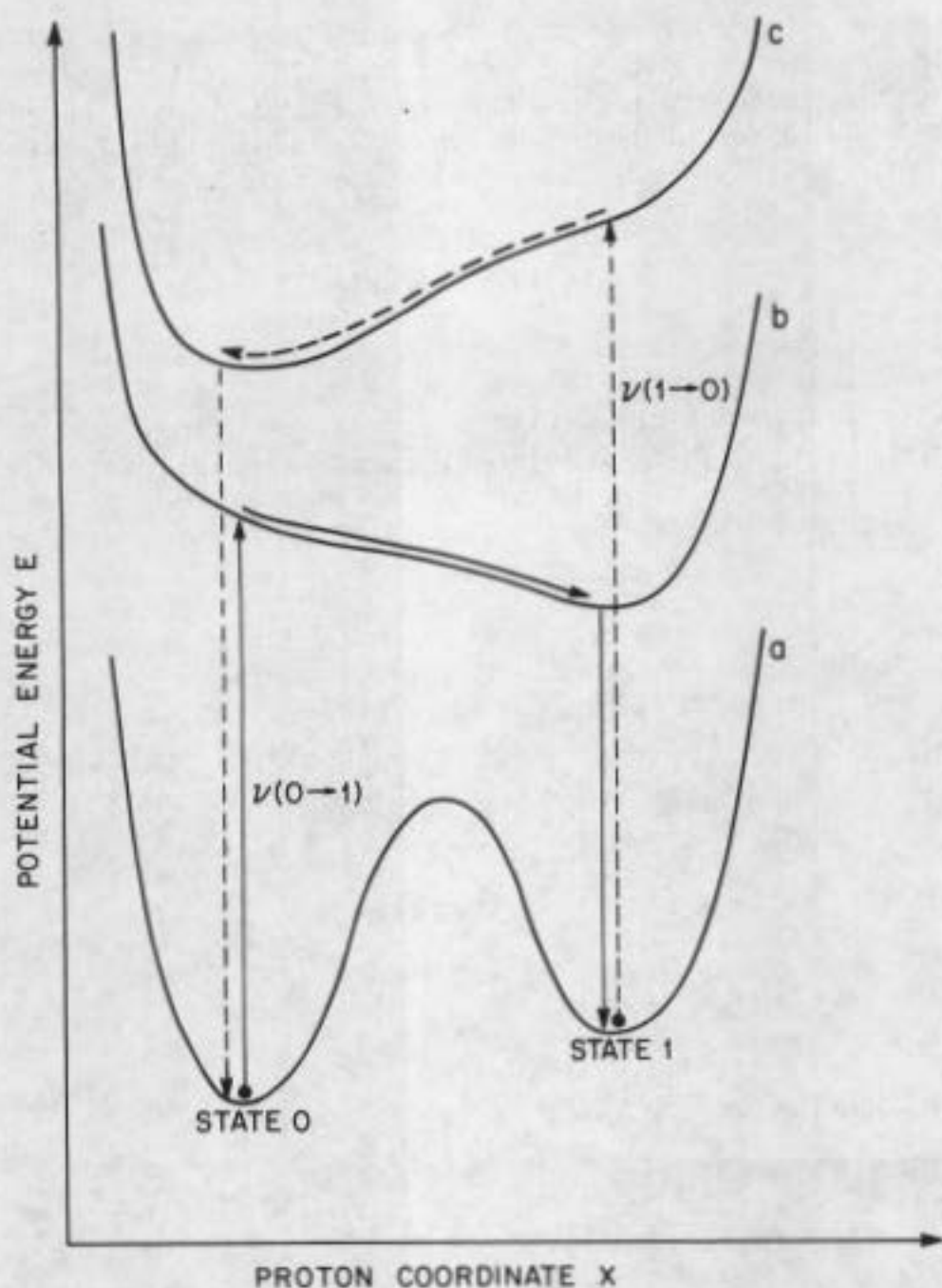


Fig. 1: Idealized photochemical switching scheme for molecules exhibiting inequivalent proton tautomers.

dashed arrows indicate the corresponding process which is initiated by radiation with frequency $\nu(1 \rightarrow 0)$. Generally $\nu(0 \rightarrow 1)$ and $\nu(1 \rightarrow 0)$ would be distinct on account of the basic asymmetry involved, so that the direction of photochemical switching could in principle be controllable. A current photochromic memory system advanced by Heller (2) operates effectively at room temperature by virtue of its holographic basis; the spectral demands in the present context would probably require elimination of absorption band overlap by cooling to very low temperature. (1)

The simple situation just described may in real applications involve considerable complication. It may be necessary to consider only weakly allowed electronic transitions in order to allow enough time to elapse in the upper states for the requisite vibrational relaxation to be effective. This would imply either weak absorptions, or intervention of intersystem crossings to yet other potential curves. However these details do not as a matter of principle eliminate the possibility of photochemical switching.

What we have just described in rudimentary fashion is a passive storage medium for information encoded in binary form. The difference in spectral absorbance for the tautomers offers the means to read out a stored message. The important question of whether one can address single molecules is an independent issue which we must leave aside for this presentation.

COUPLED SWITCHING

Figure 2 illustrates the fact that two (or more) tautomeric shifts can occur within the same molecule. Since both labile units (L) interact with the electronic structure of the entire molecule there inevitably exists a coupling between them. The excitation frequency required to switch one group depends on which state the other group is in, and vice versa. Such coupling provides the opportunity to perform information processing within a single molecule.

Let x and y represent the coordinates which describe motion of the two labile units. We are now concerned with energy surfaces in the two-dimensional x, y space and how they might serve for selective switching. In analogy with the preceding case of Section 2 we write the following expressions:

$$E_{aa}(x,y) = E_a^1(x) + E_a^2(y) + F_{aa}(x,y)$$

$$E_{ba}(x,y) = E_b^1(x) + E_a^2(y) + F_{ba}(x,y)$$

$$E_{ab}(x,y) = E_a^1(x) + E_b^2(y) + F_{ab}(x,y)$$

$$E_{ca}(x,y) = E_c^1(x) + E_a^2(y) + F_{ca}(x,y)$$

$$E_{ac}(x,y) = E_a^1(x) + E_c^2(y) + F_{ac}(x,y)$$

The first stands for the electronic ground state and the four that follow are excited states. The single-variable functions E_a^1 , E_b^1 , and E_c^1 represent for the x unit the type of curves illustrated earlier in Figure 1; E_a^2 , E_b^2 , and E_c^2 are the corresponding (but not identical!) functions for the y unit. The F_{ij} give the coupling energies between the units.

The two excitation frequencies $\nu(0 \rightarrow 1)$ and $\nu(1 \rightarrow 0)$ invoked in the previous discussion for a single tautomeric unit will now split into four frequencies, depending on the state of the other unit. The need to eliminate absorption band overlaps by cooling becomes an even more stringent matter in this case. We might denote the four resulting frequencies for switching the x unit by

$$\nu(0 \rightarrow 1, 0), \nu(0 \rightarrow 1, 1), \nu(1 \rightarrow 0, 0), \nu(1 \rightarrow 0, 1)$$

wherein we adhere to the convention that one "variable" denotes the switching event and the other denotes the state of the unit which remains unchanged. Similarly there will be four more frequencies

$$\nu(0, 0 \rightarrow 1), \nu(0, 1 \rightarrow 0), \nu(1, 0 \rightarrow 1), \nu(1, 1 \rightarrow 0)$$

for switching of the y unit. We shall presume that all eight frequencies can be rendered sufficiently distinct that they can be used in any sequence to effect the desired switchings.

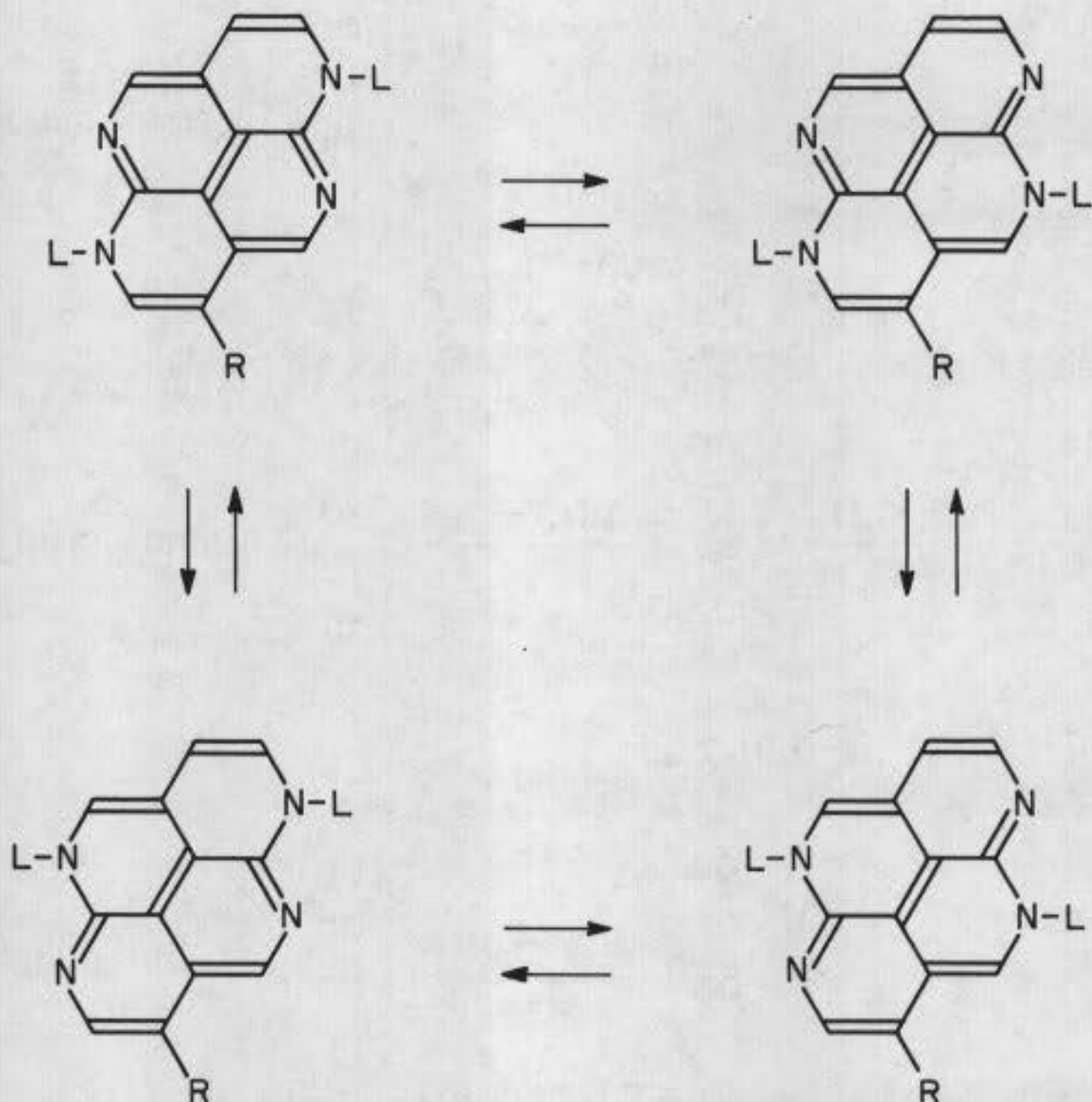


Fig. 2: Coupled shifts of labile groups (L) within a single molecule. The functional group indicated by R is present to induce asymmetry.

We now observe that adroitly chosen irradiation sequences permit a rudimentary form of information processing to be carried out intramolecularly. Starting from any one of the four binary states $(\bar{x}, \bar{y}) = (0,0), (0,1), (1,0),$ or $(1,1)$ it is possible to set \bar{x} and \bar{y} both equal to the maximum of \bar{x} and \bar{y} , or to the minimum of \bar{x} and \bar{y} , or one to the maximum and one to the minimum. The respective irradiation schemes are shown in Figure 3.

Unfortunately, it is not possible to carry out all binary operations with two-unit molecules. Three interacting units in the same molecule (see Figure 4) are required in order to carry out addition and multiplication functions for the binary codes carried by two of the three. Figure 5 indicates a five-pulse sequence that simultaneously yields the binary sum (modulo 2) and the product (i.e. logical "and") for the numbers initially borne by two units. Using the foregoing ideas the reader should be able to discover schemes for generating other binary logical operations such as "or", "nor", and "nand". It is not our purpose here to belabor the point. It is important to realize that there can be "smart molecules" capable of carrying out their own information processing *in situ*. With this concept as a backdrop it becomes crucially important to mount careful investigations of the potential energy surfaces in molecules exhibiting tautomerism. Comprehensive and precise understanding of

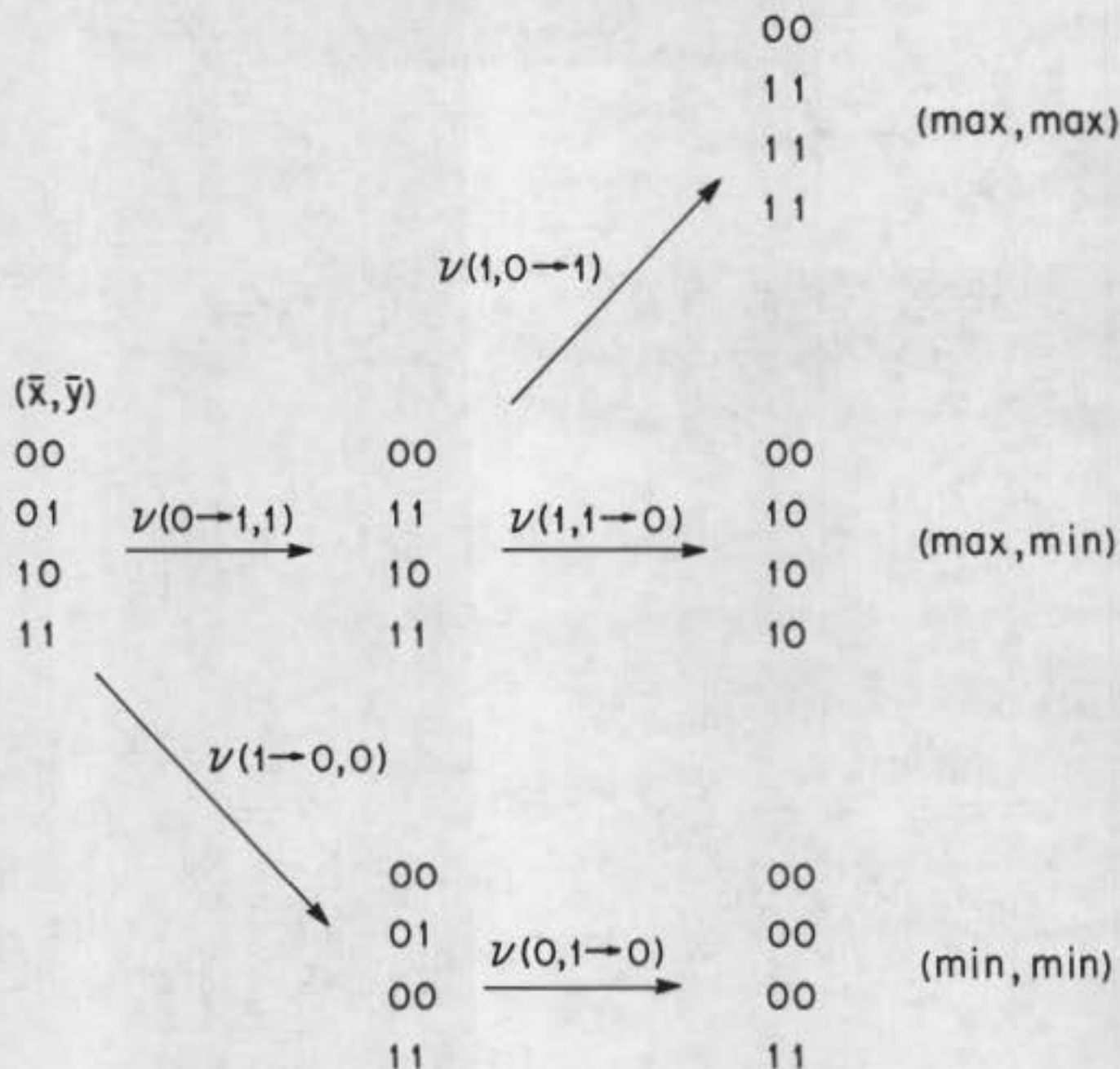


Fig. 3: Irradiation sequences to carry out binary operations within single molecules bearing two labile units.

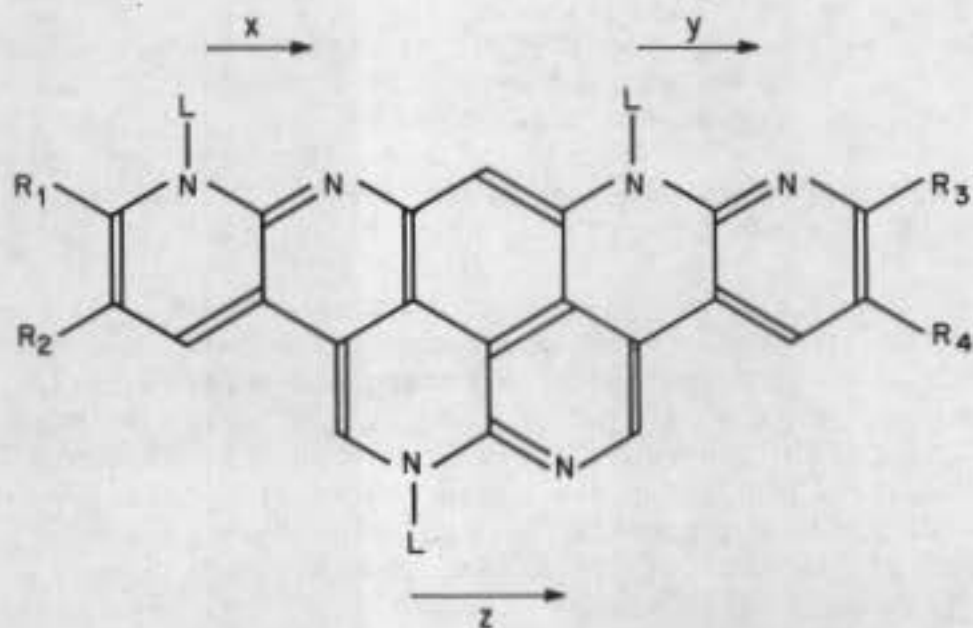


Fig. 4: Molecule possessing three labile units (L), with respective coordinated x, y, and z. The chemical groups $R_1 \dots R_4$ induce the necessary asymmetry.

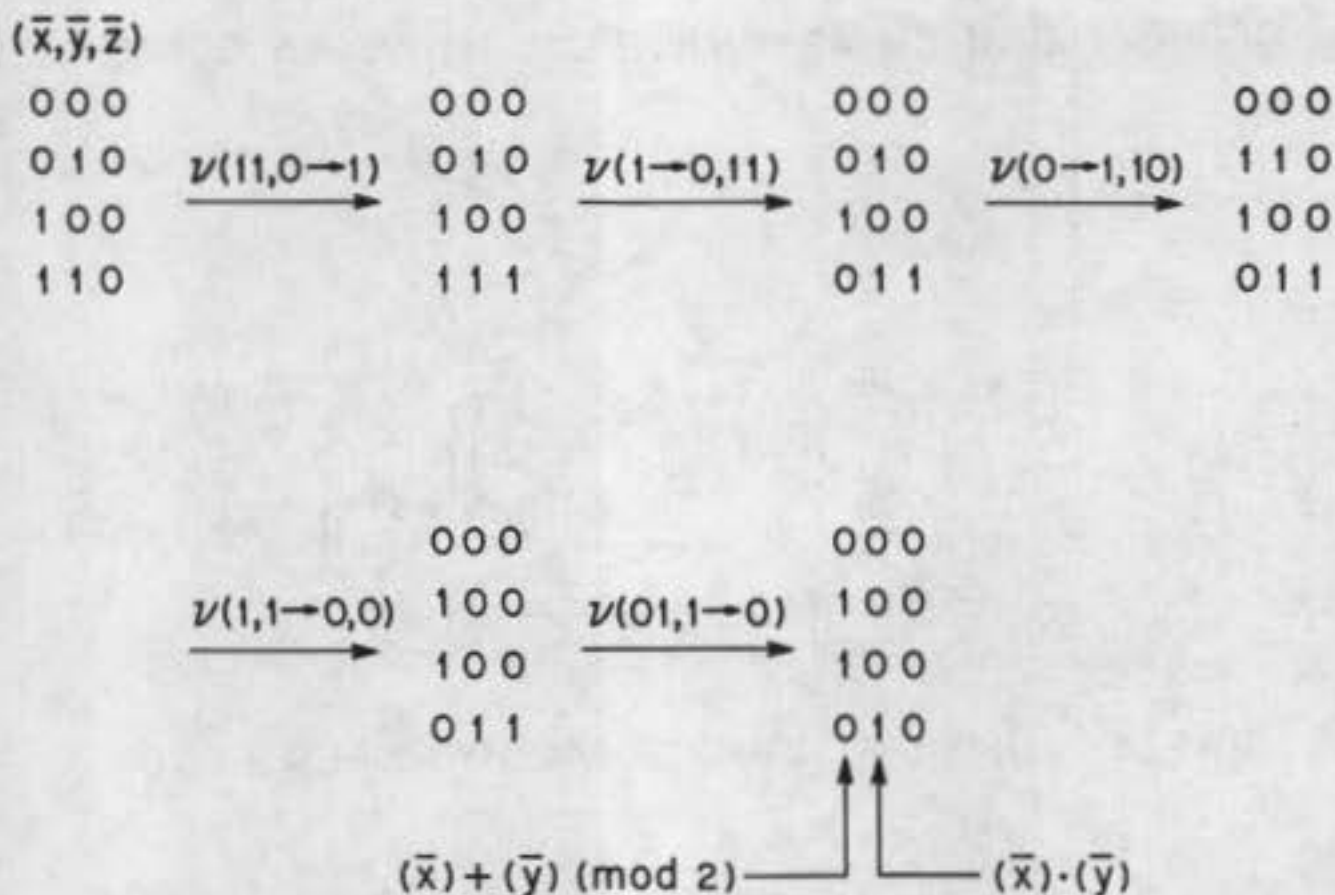
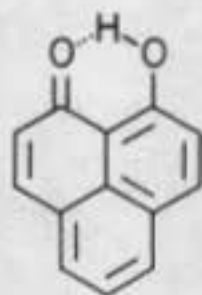


Fig. 5: Irradiation pulse sequence applicable to a three-unit molecule which effects sum and product operations.

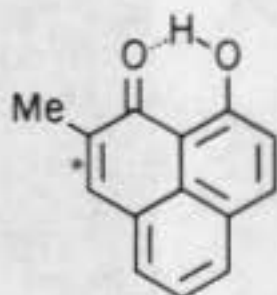
these surfaces is an obvious prerequisite to the synthesis and use of "smart molecules".

STUDIES OF HYDROGEN BONDING IN 9-HYDROXYPHENALENONES

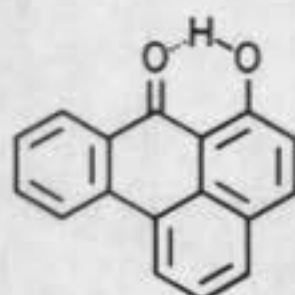
As an approach to the preceding ideas we have mounted an in-depth investigation of a class of compounds based on 9-hydroxyphenalenone (1). The parent (1) has now been extensively studied and shown to possess a strong intramolecular hydrogen bond



1



2

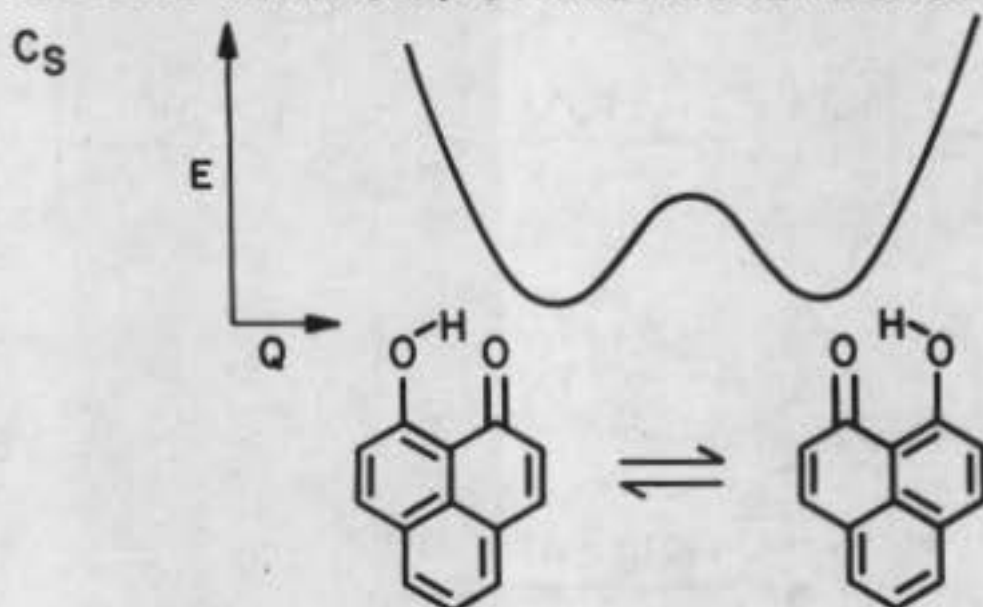


3

The first question we addressed for this molecule concerned the nature of the ground state potential surface with respect to proton motion between the two (equivalent) oxygen atoms. In particular, we wished to determine whether this surface was of the symmetric double (C_g) or single minimum (C_{2v}) type (Figure 6).

ESCA studies by Brown (3) showed that on the relevant time scale (10^{-16} sec) 1 possessed chemically inequivalent oxygen atoms (Figure 7), thus demonstrating that 1 is characterized by a double minimum ground state in the

DOUBLE MINIMUM (ASYMMETRICAL HYDROGEN BOND)



SINGLE MINIMUM (SYMMETRICAL HYDROGEN BOND)

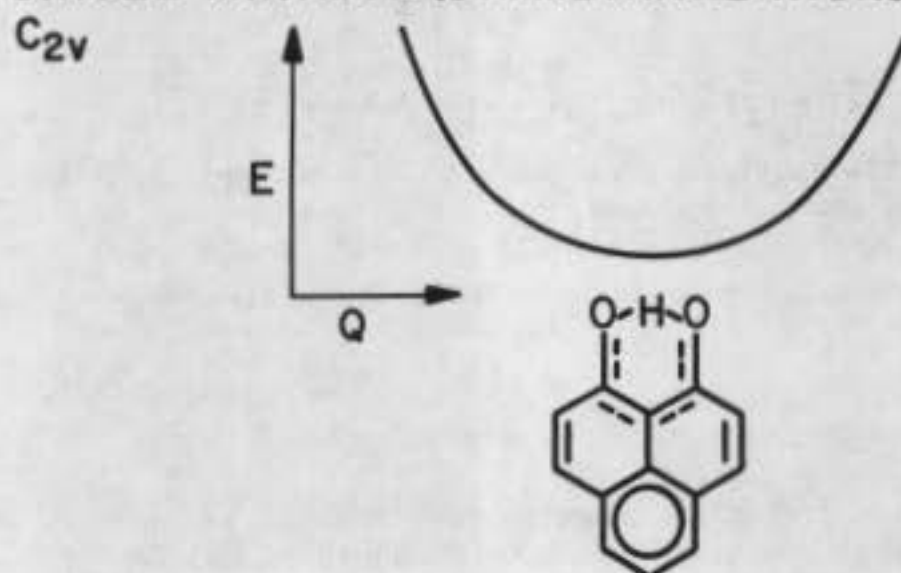
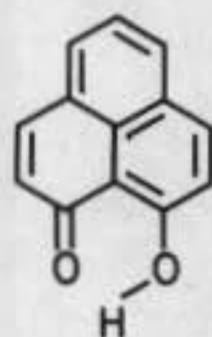


Fig. 6: Possible proton transfer potential surfaces for 9-hydroxyphenalenone (1).



O_{1s} BINDING
ENERGY (eV)

539.23

536.64

RELATIVE
AREA

1.0

0.99 ± 0.03

Fig. 7: ESCA chemical shifts for 9-hydroxyphenalenone (1) in the gas phase (from Ref. 3).

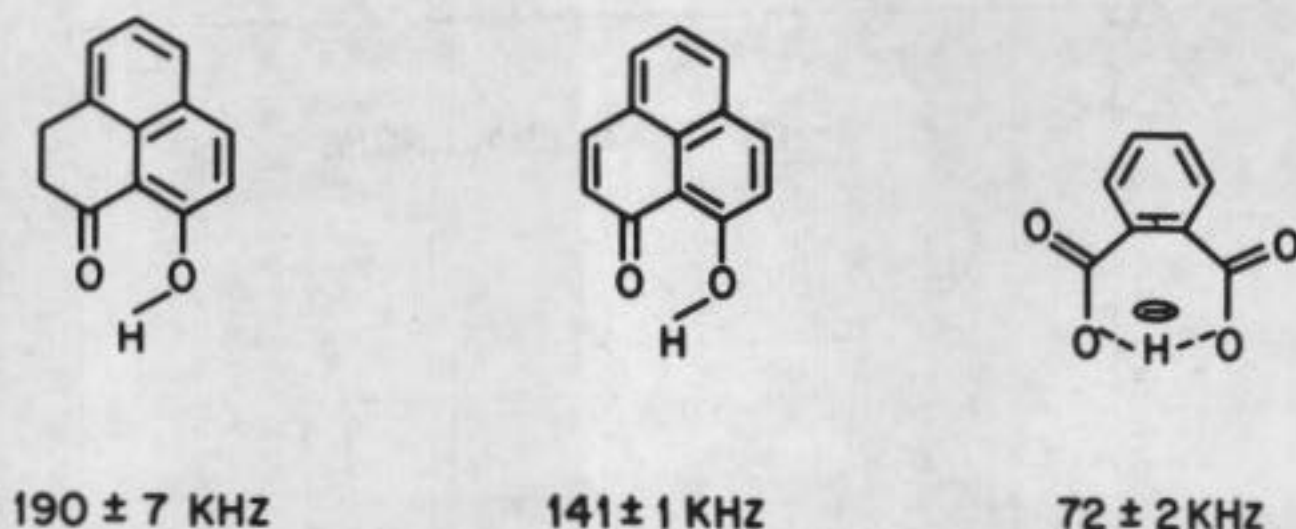


Fig. 8: DQCCs (kHz) in chloroform solution (from Ref. 4).

gas phase. Deuteron quadrupole coupling constant (DQCC) studies by Jackman (4) gave the same result for the solution state of the molecule. Figure 8 shows the DQCC's of 1 and its dihydroderivative contrasted with the value found for the symmetric hydrogen bond in the phthalate anion. An earlier X-ray crystallographic study by Svensson and Abrahams^{5,6} had found a C_{2v} structure for 1 (Figure 9), but this is presumably due to the time scale of the experiment rather than the intrinsic symmetry of the molecule: the 0...0 separation which was found in this work is characteristic of a strong hydrogen bond in a double minimum potential. Finally, a theory (7) based on the second-order Jahn-Teller (SOJT) effect provided a satisfactory rationalization of the nature of hydrogen bonding in the ground states of 1 and conjugated organic molecules in general, and is consistent with double minimum character.

At this point we turned our attention to the nature of the excited state of 1 and the relationship of the ground and excited state potential surfaces along the proton transfer reaction coordinate.

The results of the fluorescence electronic spectroscopy studies by Brus (8) are embodied in Figure 10. It may be seen that the potential barrier for proton migration in the excited state is less than a third of that in the ground state. The ground state tunneling splittings (Δ) are found to be

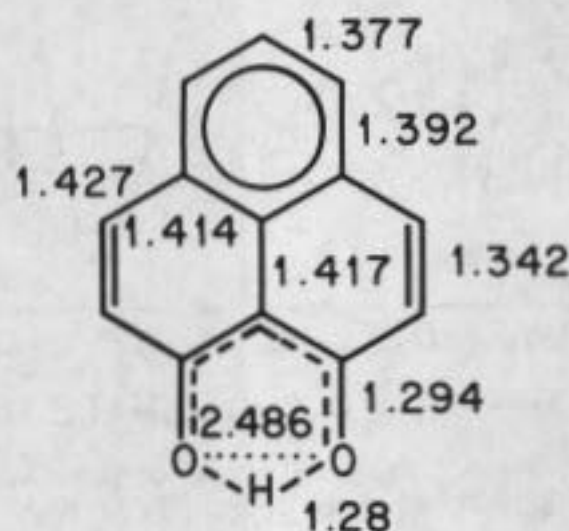


Fig. 9: X-ray crystal structure of 9-hydroxyphenalenone (1) with bond lengths (\AA) (from Ref.5).

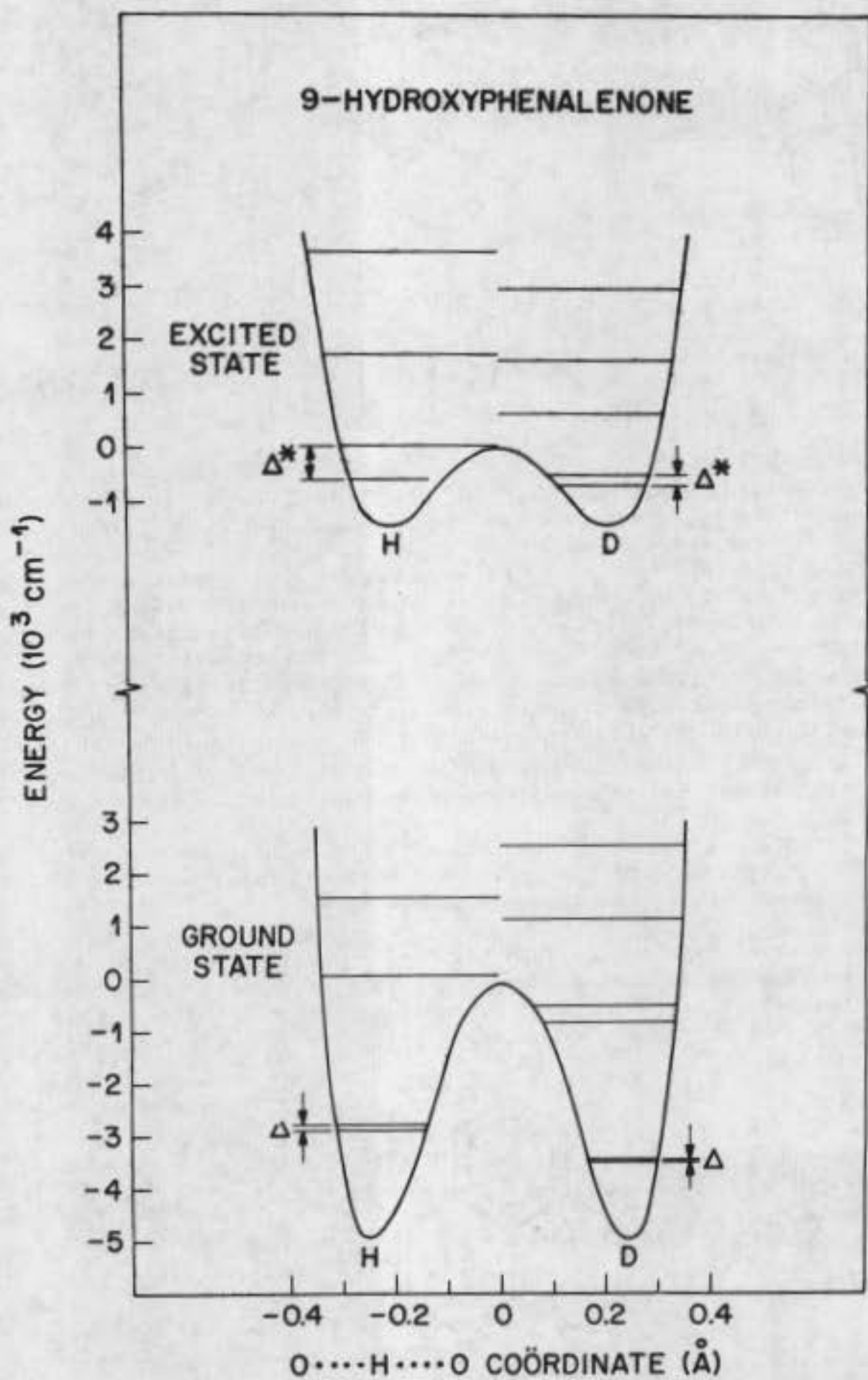


Fig. 10: Potential energy curves for 9-hydroxyphenalenone (1) derived from electronic spectroscopic studies (from Ref. 8).

$\underline{1}$ -h = 130 cm^{-1} and $\underline{1}$ -d = 10 cm^{-1} , which lead to tunneling times (τ) of: $\underline{1}$ -h = 0.13 psec and $\underline{1}$ -d = 1.7 psec (assuming coherent oscillation of the nucleus between potential minima). The excited state tunneling times (τ^*) are found to be: $\underline{1}$ -h = 0.02 psec and $\underline{1}$ -d = 0.09 psec.

Recent studies (9) of the unsymmetrical 2-methyl-derivative (10) (2) have shown that the potential minima are split by $\sim 200 \text{ cm}^{-1}$ in this compound. This splitting is sufficient to substantially localize the nuclear wave function in the ground state of 2, but not in the excited state. Studies on related molecules where the asymmetry is more pronounced (such as 3 (11)) are currently in progress.

The work to date has allowed a fairly complete characterization of the potential surfaces of 1 and related compounds. Proton transfer via tunneling has been shown to be very fast in these compounds. It seems likely, however, that a more massive group will have to be substituted for the proton if usable memory phenomena are to be observed in these compounds. The trimethylsilyl derivative of 1 (12) has been shown to possess a ground state potential barrier of the same order of magnitude as that found in 1, and may be useful in this connection.

The synthetic effort to produce these molecules, and the experimental studies thus far devoted to their spectroscopic characterization, constitute only the beginning of a long term project. We expect in the near future to expand the set of available tautomeric molecules, to improve the state of knowledge of their ground and excited state potential surfaces, and to examine quantum yields for photochemical switching. Only by concerted effort in all these directions will materials be identified with acceptable performance as molecular memories.

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DISCUSSION

Dr. Shipman: ANL - If you have tunneling back and forth between two wells in a picosecond or so, how are you going to keep the bit tripped in the state where you want it? Unless you have a computer that can carry out a calculation in much less than a picosecond it is not going to do you much good.

Dr. Haddon: I think ultimately to retain the integrity of the information, one is going to have to go to a more massive mobile group such as trimethylsilyl.

Prof. Ratner: NW Univ. - That structure that you have, involving essentially a 2.5 Å hydrogen bond, is very reminiscent of the old work that Rundle did. In systems where he replaced hydrogen with the deuterium, not only did the hydrogen to oxygen distance change, but the oxygen to oxygen distance also changes in those cases by as much as 0.01 to 0.06 Å. That can result in essentially a completely different spectroscopic characterization. Have you determined the deuteride structure, too, or just the proton structure?

Dr. Haddon: Just the proton structure. Are you suggesting that the structures would be significantly different?

Prof. Ratner: Yes. There are a number of well-documented examples. The standard one is something called chromous acid.

Dr. Haddon: Right. Of course, 9-hydroxyphenalenone is a constrained system.

Prof. Ratner: So are those, or some of them. The chromous acid is not, but I think oxalic acid was the same sort of thing.

Dr. Haddon: We have studied the 9-butoxy. The hydrogen is replaced with a butyl group so that the hydrogen bonding is removed, and we find that the oxygen-oxygen separation opens up from 2.49 to approximately 2.64 Å, so I don't think that there is a great deal of flexibility in this system.

Dr. Siedle: 3M - During the analogue of the system, the phena and hydrogen pentazene system, if the nature of the constituents are high powered, there may be a charge transfer. It would be interesting to speculate. If you start moving those hydrogens that are now bonded to nitrogen instead of oxygen, there might be a significant change in the optimal spectrum.

Dr. Haddon: Yes.