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Reminiscences of a menage a trois. The true story of the development of Salem's theory of organic photochemistry^{1,2}

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Abstract

A personal recollection of the beginning of Lionel Salem's theory of a 'classification of photochemical reactions' is presented. The classification was developed by a collaborative effort led by Lionel Salem and assisted by N.J. Turro and W.G. Dauben. © 1998 Elsevier Science B.V.

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The truth can now be told that during the first half of the 1970s, Lionel Salem and I participated in an intellectual 'menage a trois' together with Bill Dauben, Professor of Chemistry at Berkeley. The actual beginning was during the period of 12–18 July 1970 at the Third IUPAC Symposium on Photochemistry held at St. Moritz, Switzerland: a conference that I did not attend. I learned from participants that the meeting featured an informal, spontaneous and exciting discussion and debate on the question, 'What is a diradical?' by two of the dominant figures in the field, George Hammond and Lionel Salem. Although I was not present at the Hammond–Salem debate, the written discussion and the topic of 'what is a diradical' turned out to have a major impact on my career and my intellectual perceptions of how photochemical reactions occur.

At the Fourth IUPAC Symposium on Photochemistry, held in Baden-Baden, Germany during 16–22 July 1972, the lecture hall was very high-tech and the audience sat two to a desk with a shared microphone available for asking questions after each lecture. I sat next to Lionel on a number of occasions, and during the 'organic lectures', he would needle me about the lack of discipline that existed in the writing of organic photochemistry reaction mechanisms. He felt that 'anything goes' was the rule used to explain the seemingly endless variety of reaction products that were being discovered in those early days of many exciting discoveries in organic photochemistry. During the Symposium, Lionel presented an outstanding lecture on diradicals [1]. After the lecture, we had a remarkably fruitful discussion in which some of my naive ideas concerning the orbital interpretation of the reason for efficient triplet formation in the thermal decomposition of dioxetane had a splendid theoretical basis in Lionel's concepts of topicity! This was exciting stuff!

¹ Dedicated to Lionel Salem on the occasion of his 60th birthday.

² Following the death of W.G. Dauben earlier this year, I would also like to dedicate this reminiscence to his (W.G. Dauben's) memory.

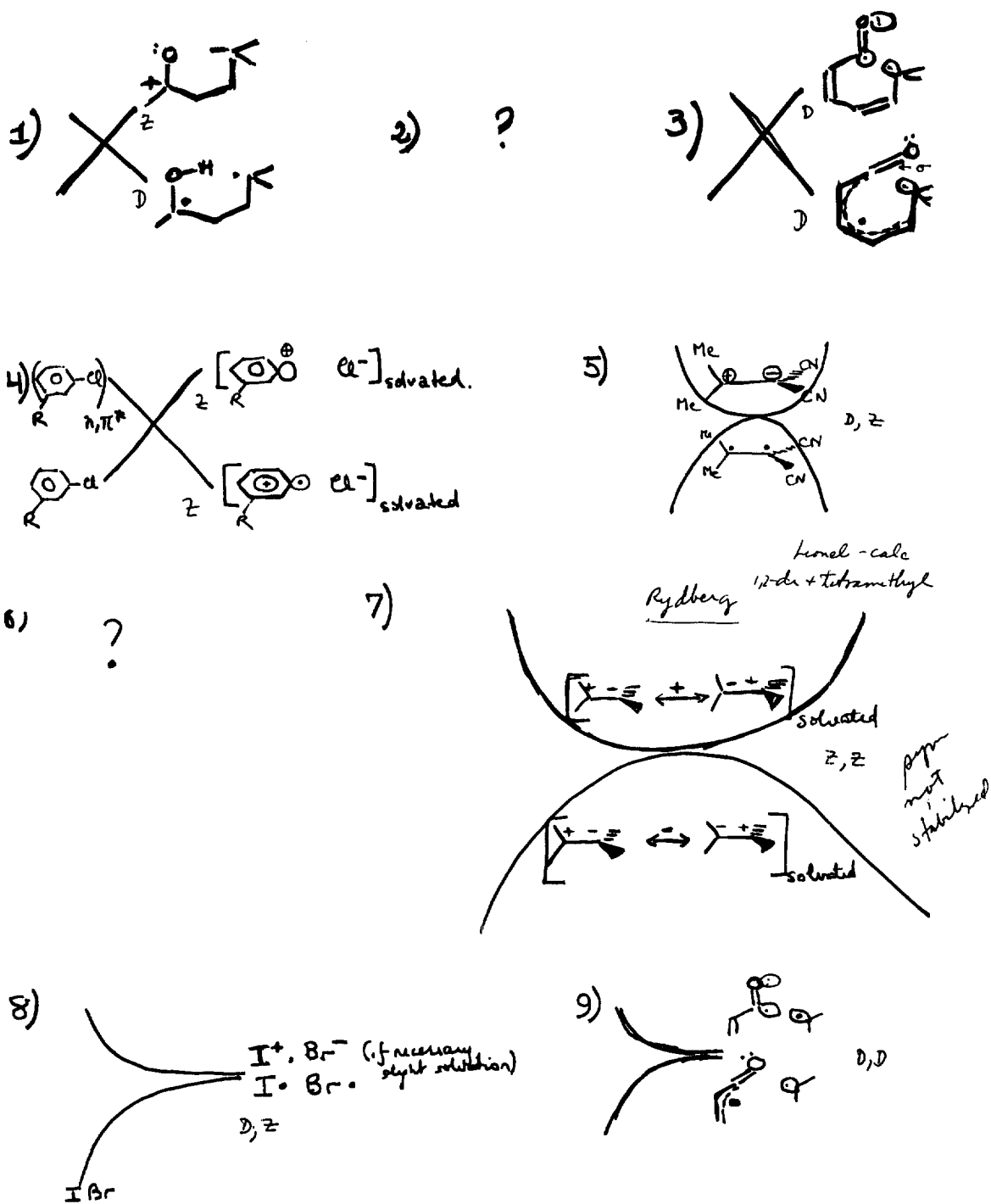
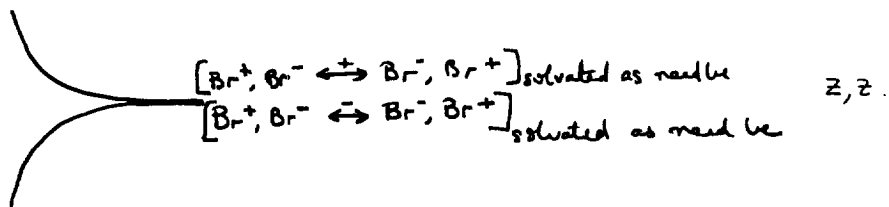
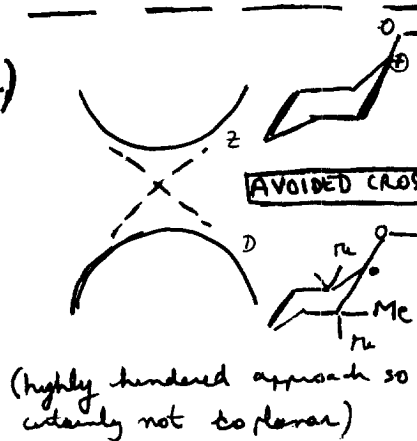


Fig. 1. Lionel's surface classifications 1-9.

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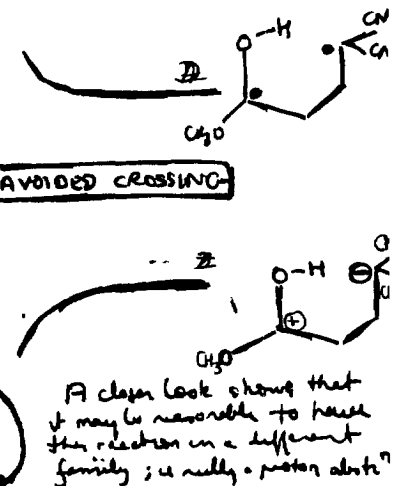


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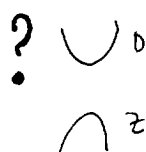
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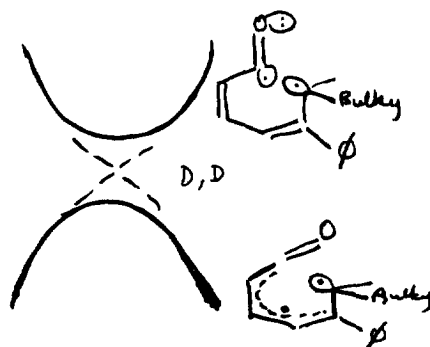
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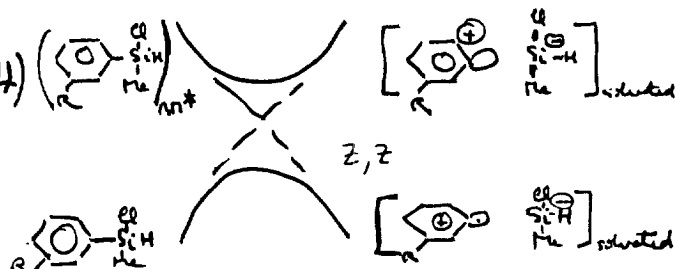
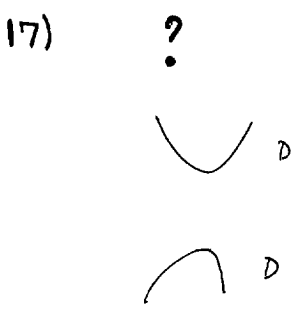
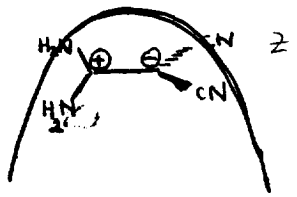
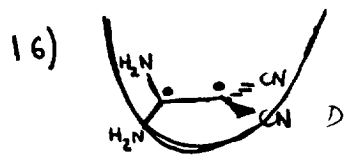
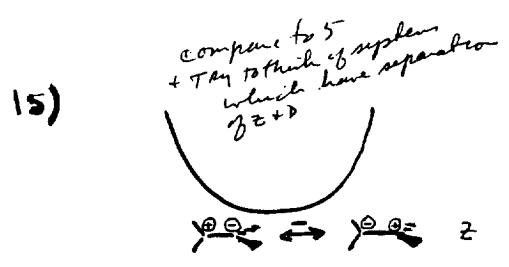
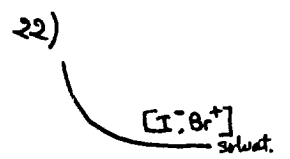
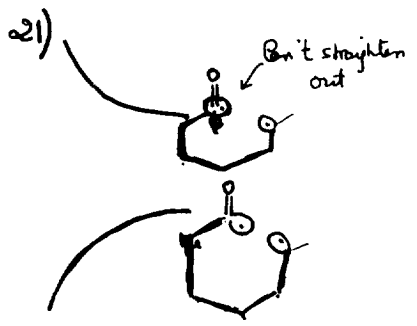
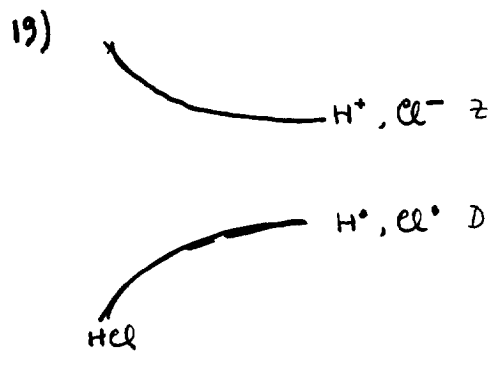
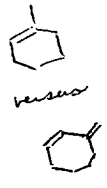


Fig. 2. Lionel's surface classifications 10-14.



approach of H+ to I=C⁺ does this do it? in CH₃OH



20) See p. 2

Fig. 3. Lionel's surface classifications 15-22.

At the very end of the conference, Lionel, Bill Dauben and I had a beer at the hotel as we were waiting for transportation to the airport. Lionel now was needling both Bill and myself about the lack of coherence in the mechanisms and theory of organic photochemistry. Bill and I retorted with, "Lionel, you're just the person to do something about this unfortunate state of affairs!" Lionel retorted by challenging us to join him in a venture to seek the framework of a coherent theory. German beer, with its ability to produce *gemütlichkeit*, had produced the atmosphere for a partnership that was to be exceedingly stimulating and informative for all three of us.

During the week of 6–10 August 1973, at the Gordon Conference on Organic Photochemistry at Tilton, New Hampshire, Lionel Salem presented another outstanding lecture on diradicals emphasizing the possibilities of excited state reactions being either heterolytic or homolytic pathways, but couching reaction mechanism in the context of energy surfaces. Lionel and I had an opportunity to follow up on our discussions of the theory of photoreactions, but Bill Dauben was unfortunately not able to attend the Conference. Nevertheless, it was determined that the 'menage a trois' must move forward with the sacred pledge we had made over spilt beer in Baden-Baden the year before. One afternoon, while he ate a strawberry shortcake and I ate a hot fudge sundae at an ice cream shop in greater downtown Tilton, Lionel wondered if some simple rules, employing the ideas of surface correlations, could be used to examine organic photoreactions, especially reactions of the ubiquitous n, π^* excited states. This seemed like a very exciting possibility to me. Perhaps in the same way that organic chemists write lines and connections so profitably to describe molecules, an extension of the idea of connections could be created to describe reaction steps. For example, we speculated that there may be a relatively small number of a-priori possibilities based on the simple notions of 'perfect crossing', 'perfect avoiding' and 'contact' of energy surfaces. Bill was informed of this progress and it was determined that we would meet with Lionel in Orsay and work like mad for a month, just before the 5th IUPAC, which was to be held in Enschede, The Netherlands during 21–27 July 1974.

Before the IUPAC meeting, there would be one opportunity for me to meet with Lionel during the

Fall of 1973 and to work with him on the preliminary aspects on the theory. By the time I arrived in Paris, he had already discovered over 20 families of surfaces types, which depended on the number of radical centers and which can be seen, in Lionel's inimitable handwriting, in Figs. 1–3. At that point, we were able to document real examples of 18 or the 22 types. This was very exciting, but the simplicity I had hoped for was not apparent. We communicated the results to Bill Dauben and then prepared for our meeting in Orsay. Lionel was very excited about these ideas and keen to get something out quickly. The results of these discussions and correspondences led to a short note written by Lionel entitled 'Surface Crossings in Photochemistry' [2] in which he pointed out the use of a symmetry plane to classify orbitals and to serve as the basis for energy surface diagrams.

When Bill and I met Lionel in Orsay in the summer of 1974, he proudly handed us a 38 page draft which was to serve as a basis for a manuscript to be submitted to *Accounts of Chemical Research*. The first sentence of the draft was "Classification has been the dream of Chemists for centuries". This sentence was one of the few things left unchanged in the final paper! During three weeks of exhilarating daily meetings and brainstorming and some fabulous French meals, the 'menage' produced the classification of photochemical reactions that appeared in the *Accounts* article [3]. Lionel was extremely excited about the successful collaboration that had resulted and the 'menage' went on to enjoy a splendid IUPAC meeting in Eschede and discuss our ideas with many of our colleagues at that symposium.

At the 6th IUPAC meeting on photochemistry at Aix-en-Provence, France, during 19–23 July 1976, a workshop on the use of Lionel's theory of photochemistry was held and the concepts of applying energy surfaces and surface correlation diagrams for the understanding of photochemical reactions began to be accepted by the community as an integral part of the photochemical paradigm. By the time of the 7th IUPAC meeting on photochemistry in Leuven, Belgium in 1978, Lionel's theory was incorporated into a number of lectures and presentations.

During the 1970s, Lionel and I had continuous contact sharing ideas about how his theory of

photoreactions could be generalized and expanded. In the revision of my textbook, Lionel's ideas held a dominant role in organizing the discussion of photochemistry and photophysics and provided the intellectual scaffolding for a systematic and rational organization of everything photochemical. A casual perusal of the text will reveal 'Salem diagrams' to explain (in a theoretically disciplined and precise fashion!) the mechanisms of a range of photochemical reactions.

Lionel Salem has provided the driving force in the development of energy surface theory of photoreactions. Bill Dauben and I have enjoyed the effort because of the pure delight of being able

to merge and share, firsthand, Lionel's remarkable imagination and creativity. Both Bill and I were extremely fortunate to take part in a very special intellectual and scientific adventure and collaboration that comes all too infrequently in spite of good intentions.

References

- [1] L. Salem, *Pure and Applied Chemistry* 33 (1973) 313.
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- [3] L. Salem, N. Turro, B. Dauben, *Accounts of Chemical Research* (1974).