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Review Article

Disulfides, Indene and Bergson

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Dedicated to Professor Göran Bergson on the occasion of his 65th birthday

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Molecular orbital theory for the disulfide bond is reviewed and establishes the lasting impact of Göran Bergson's pioneering effort. Intramolecular proton transfer in indene and substituted indenes is reconsidered in an attempt to shed light on the effects of a basic environment.

Göran Bergson visited the first Löwdin Summer School at Vålådalen on a short leave from his military service in August 1958. We had known each other fleetingly from the morning lectures by Löwdin in the spring and a friendship developed around our common interest in quantum chemistry and its application towards the description of experimental phenomena. Göran was ready to subject himself to the rigmarole of the Uppsala style doctoral dissertation in May 1962 and kindly selected me as one of his personal opponents to follow Lennart Schotte, the Faculty opponent. Schotte agreed that I should concentrate on the theoretical sections of the thesis, the only parts I could have an opinion on. Thus I got a thorough exposure to the molecular orbital model that Bergson introduced to relate strain energy in ring compounds with disulfide bonds to observed red shifts[1] in absorption.

Arne Fredga's new docent embarked on a new line of research which proved challenging and fruitful. Intramolecular proton transfer in indenes has had his attention ever since, to a greater or lesser degree. A series of papers was initiated[2] and the kinetics as well as mechanisms related to the proton mobility were examined. There were a few discussions between us, but I could not at the time contribute since I was heavily involved with my own thesis work. Our geographical locations shifted thereafter and there was more than a decade during which our scientific paths were quite separate. The most recent decade has seen our interests converge somewhat again and the description of the 1-methylindene isomerization to 3-methylindene is still an unresolved issue to a certain extent.

My tribute to Göran Bergson contains a section of some further applications of the disulfide bond model to optical activity. It is followed by a part where the indene system is mapped onto a quantum chemical model. Conclusions complete the paper.

Bergson's disulfide bond model

Two bonded sulfur atoms in a molecular framework contribute a set of two loosely bound, lone pair orbitals, and it was Bergson who realized that these overlap to a greater or lesser extent dependent upon the dihedral angle of the arrangement. He considered systems of the kind R–S–S′–R′ and chose in the first analysis[3] the 3pπ orbitals of the sulfur atoms with nodal planes R–S–S′ and S–S′–R′ respectively as representative of the lone pairs. The overlap of the two is proportional to the cosine of the dihedral angle ϕ between the nodal planes in Fig. 1.

Bergson followed Mulliken's notions[4] and formed bonding and antibonding combinations with orbital energies

$$\varepsilon_{\pm} = \frac{\alpha \pm \beta}{1 \pm S} = \alpha \pm \frac{\beta - \alpha S}{1 \pm S} \qquad (1)$$

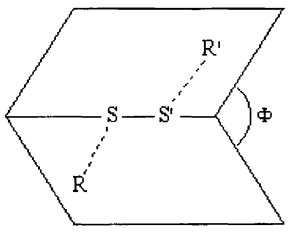

Fig. 1. Definition of the dihedral angle ϕ for the disulfide bond.

where the coupling parameter β and the overlap integral S both have a factor $\cos(\phi)$ from the dihedral angle ϕ while the atomic parameter α is considered independent thereof. The presence of the overlap is essential here, both orbitals are occupied in the normal state and within the assumption that the total energy is represented by the sum of the orbital energies he found that ground state energy increases with overlap according to eqn. (2)

$$E = 2\varepsilon_+ + 2\varepsilon_- = \frac{4(\alpha - \beta S)}{1 - S^2} = 4\alpha - \frac{4S(\beta - \alpha S)}{1 - S^2} \qquad (2)$$

since $\beta < \alpha S$ with common estimates and orbital phases. Bergson argued that the observed red shift for smaller angles from the disulfide chromophore arose from the increase of the orbital energy of the antibonding combination. This implies that the excited system has a formal hole in the antibonding orbital and an electron in an antibonding σ-type orbital with little or no dependence on the dihedral angle. It follows that the strain energy relative to the minimum energy perpendicular conformation relates to the redshifts as

$$E(\phi) = E(\pi/2) + \frac{4S_0 \cos(\phi)[h\nu(\pi/2) - h\nu(\phi)]}{1 + S_0 \cos(\phi)} \qquad (3)$$

in terms of the observed excitation energy $h\nu(\phi)$. The maximum overlap integral, for parallel orbital axes, is given as S_0. This simple formula provided an excellent link between spectroscopy and thermochemistry. It was also valid for generalizations to hybrids.[5]

Disulfides were again brought to my attention by Göran Claeson.[6] He was concerned with the optical activity, or lack thereof, in 1,2-dithianes. Rules had been formulated for the sign of the rotatory strength of the first band in the ultraviolet spectrum in ring compounds and it was anticipated that circular dichroism spectra would be useful for the identification of conformations around disulfide bonds. Josef Michl who had joined me at Aarhus in 1968 investigated the predictions that would be a consequence of Bergson's model. The analysis bore out that the sign of the rotatory strength would have a quadrant rule that was negative for dihedral angles on the intervals $(0, \pi/2)$ and $(\pi, 3\pi/2)$, with positive values elsewhere. Elementary calculations within the Complete Neglect of Differential Overlap model,[7] supplemented with a rule for the matrix elements of the dipole velocity[8] and the magnetic moment operator, supported this analysis.[9]

Proton transfer

Unimolecular isomerization reactions offer particular challenges for the theoretically inclined investigator. Two or more bonds are broken and formed, and transition state structures are rarely well characterized by molecular orbital configurations or valence bond structures, yet there is no physical separation of active groups in the process. The conversion of 1-methylindene to 3-methylindene through base-catalysis became a prominent field of study for Göran Bergson as a young docent and as the first professor of organic chemistry at the new University of Umeå. He and his collaborators determined kinetic data and the stereochemical features of the process. They suggested that the proton is 'lifted' by the base lone pair and deposited at the final site. Theoretical confirmation of this view is not strong. Even rather extensive calculations[10] provide little insight regarding the bonding in the system and the characterization of the reaction path. A 'minimal' model for the electronic system is outlined below in terms of a (4+1)-orbital basis and a (2+2)-dimensional state basis.

Four orbitals are considered as the 'active' ones in the analysis. They are the π-orbitals on the three carbons in the five-membered ring that are not part of the six-membered one and the hydrogen orbital of the moving atom. Orbitals ξ, η and ζ refer to the 1, 2, and 3-carbons respectively and h represents the hydrogen orbital. The base contributes an orbital b as indicated in Fig. 2. The most primitive valence bond structure considers the electronic wavefunction for the reactant, 1-methylindene, as having spin pairing between ξ and h as well as between η and ζ. Similarly the product state, 3-methylindene, is represented by the spin pairings (ξ, η) and (ζ, h). These two state functions are not orthogonal even if the orbitals are assumed to be. A useful basis for the description of both the reactant and the product valence bond wavefunction is in terms of an intermediate set of structures:

$$|I\rangle \equiv |^1(\xi\zeta)^1(\eta h)\rangle;\ |T\rangle \equiv |^3(\xi\zeta)^3(\eta h)\rangle;$$

$$|R\rangle = |I\rangle\frac{1}{2} - |T\rangle\frac{\sqrt{3}}{2};\ |P\rangle = |I\rangle\frac{1}{2} + |T\rangle\frac{\sqrt{3}}{2} \qquad (4)$$

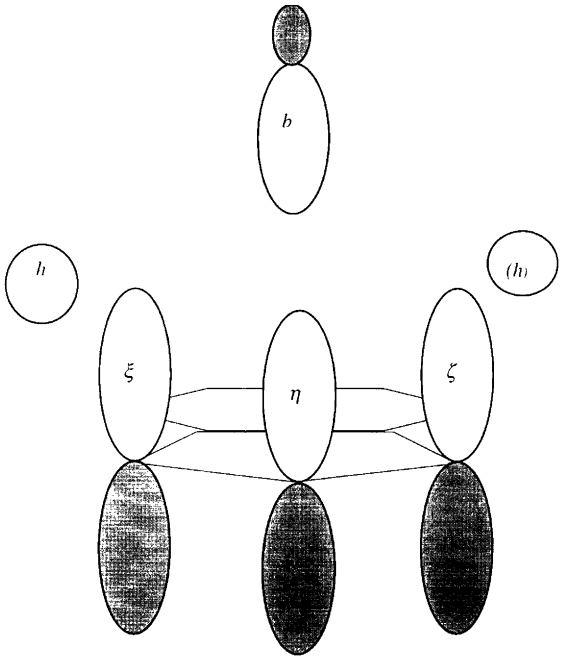

Fig. 2. Notations for the active orbitals in the indene system: carbon π-orbitals are ξ, η, and ζ, the lone-pair base orbital is b, while h and (h) indicate the hydrogen orbital in the initial and final position, respectively.

where the notation indicates that the I-state has spin-pairing between ξ and ζ orbitals and between η and h, and the T-state has the same sets triplet coupled while combining to a total singlet. These two states are orthogonal, provided that the orbitals are. The R-state and the P-state represent the initial and final situation in the reaction as indicated previously:

$$|R\rangle = |^1(\xi h)^1(\eta\zeta)\rangle; |P\rangle = |^1(\zeta h)^1(\xi\eta)\rangle \tag{5}$$

A general state within the manifold has the form

$$|S\rangle = |I\rangle \cos\sigma + |T\rangle \sin\sigma(\cos\tau + i\sin\tau) \tag{6}$$

with the option of a complex phase anticipated. It is seen that the reactant state corresponds to either $(\sigma, \tau) = (-\pi/3, 0)$ or $(\sigma, \tau) = (\pi/3, \pi)$. The product state may be represented similarly by $(\sigma, \tau) = (\pi/3, 0)$ or by $(\sigma, \tau) = (-\pi/3, \pi)$. Other representations are obtained by transformations $\{\sigma \to \pi - \sigma;\ \tau \to \pi + \tau\}$ which indicates that states may be mapped onto points of the unit sphere in three dimensions, S_2.

A two-state formulation seems to offer a means to describe the transition from the reactant to the product in the current problem but fails to indicate the postulated participation of a base to catalyze the reaction. Ion formation would involve abstraction of the relevant proton and a reorganization of the electronic structure. Thus it would make the singly occupied hydrogen orbital available to coupling with the base orbital b. Each of the two basis states has a partner where the role of the h and the b orbitals is interchanged. These couple to each other in the same way as the I and the T states do and have interaction elements with the latter.

Matrix elements of the electronic Hamiltonian are expressed in terms of the so-called Coulomb and exchange integrals when a valence bond formulation applies.[11] A useful and compact notation is offered by complex basis states defined as eqn. (7).

$$|h\rangle = |I\rangle\sqrt{\tfrac{1}{2}} + |T\rangle i\sqrt{\tfrac{1}{2}}; |\tilde{h}\rangle = |I\rangle\sqrt{\tfrac{1}{2}} - |T\rangle i\sqrt{\tfrac{1}{2}} \tag{7}$$

The label h indicates that the hydrogen orbital is singly occupied. The additional states will be similarly denoted as $|b\rangle$, $|\tilde{b}\rangle$ so that the base orbital is singly occupied while the hydrogen one is doubly filled. Coulomb integrals are denoted as

$$\langle h|H|h\rangle = \langle\tilde{h}|H|\tilde{h}\rangle = \alpha_h; \langle b|H|b\rangle = \langle\tilde{b}|H|\tilde{b}\rangle = \alpha_b \tag{8}$$

while resonance integrals are

$$\langle h|H|\tilde{h}\rangle = \langle\tilde{h}|H|h\rangle^* = \beta_h; \langle b|H|\tilde{b}\rangle = \langle\tilde{b}|H|b\rangle^* = \beta_b \tag{9}$$

and coupling elements are

$$\begin{aligned}\langle h|H|b\rangle &= \langle b|H|h\rangle = \langle\tilde{h}|H|\tilde{b}\rangle = \langle\tilde{b}|H|\tilde{h}\rangle = \gamma_b \\ \langle h|H|\tilde{b}\rangle &= \langle\tilde{b}|H|h\rangle^* = \langle\tilde{h}|H|b\rangle^* = \langle b|H|\tilde{h}\rangle = \gamma_b\end{aligned} \tag{10}$$

Traditional notation[12] provides the expression for the resonance integral β_h as

$$\beta_h = -(\xi\zeta) - (\eta n) + [(\xi h) + (\eta\zeta)]\frac{1 + i\sqrt{3}}{2} + [(\xi\eta) + (\zeta h)]\frac{1 - i\sqrt{3}}{2} \tag{11}$$

in terms of effective exchange integrals[13] between the indicated orbitals. The complex value of this element is the sum of three numbers which differ in phase by $2\pi/3$ and the lengths of which are determined by the particular bonding situation for the hydrogen. The ground state energy equals $\alpha_h - |\beta_h|$ when coupling to the base orbital is ignored, and the state vector is $|0\rangle = [|h\rangle - |\tilde{h}\rangle\beta^*/|\beta|]\sqrt{1/2}$. It is readily confirmed that an expansion in I- and T-states gives real coefficients.

A full four-state treatment involves three real and three complex parameters and becomes rather involved. It is preferable to consider a perturbation approach and consider the set $\{\beta_h, \gamma_b, \beta_b\}$ as having small values. The unperturbed problem has two degenerate energy levels:

$$\alpha = \tfrac{1}{2}\{\alpha_h + \alpha_b \pm \sqrt{(\alpha_h - \alpha_b)^2 + 4\gamma_h^2}\} \tag{12}$$

and the degeneracy is removed by first order perturbation theory involving an effective complex matrix element. Thus an estimate of the ground state energy will have the form

$$\begin{aligned}\varepsilon &= \alpha_h - |\beta| - \tfrac{1}{2}\{\sqrt{(\alpha_h - \alpha_b)^2 + 4\gamma_h^2} - \alpha_b + \alpha_h\}, \\ \beta &= -\beta_\eta + \beta_\xi\frac{1 + i\sqrt{3}}{2} + \beta_\zeta\frac{1 - i\sqrt{3}}{2},\end{aligned} \tag{13}$$

with a notation for the three new, effective exchange parameters which indicates the preferred bonding site for the hydrogen. The numerical values of these change along the reaction path. Stabilization of the system through the interaction with the base is represented by the last term in the energy expression but influences the β-value as well.

It is a significant feature of the energy form (13) that the norm of β is present. The energy surface will exhibit a conical intersection whenever the three coefficients, $\{\beta_\xi, \beta_\eta, \beta_\zeta\}$, are equal. Such a special point may influence the phase relations of the electronic wavefunction in significant ways[14] and needs attention in reaction processes even if the energy region at an exceptional point is inaccessible. One observes further that the state vector is not analytic at the point of conical intersection. The limited domain of molecular configuration space considered here permits a mapping onto a limited domain of the three-dimensional space with coordinates $\{\beta_\xi, \beta_\eta, \beta_\zeta\}$. The conical intersection is then a line rather than a single point. A related mapping was used by Davidson[15] in order to analyze degeneracy features in triatomics.

The energy expression (13) can be considered as a function of the three β-variables and the Coulomb integral α_h may be assumed to be a continuous function with

at least two derivatives so that a Taylor series representation is relevant. A second degree form is relevant in order that the total energy surface should exhibit minima at the reactant and product conformations and a stationary point at some intermediate form. One possibility for such an expression is given in eqn. (14)

$$\varepsilon = \alpha - |\beta| + \frac{(3\beta_\xi - \beta_\xi^0)^2}{12|\beta_\xi^0|} + \frac{(3\beta_\eta - \beta_\eta^0)^2}{12|\beta_\eta^0|} + \frac{(3\beta_\zeta - \beta_\zeta^0)^2}{12|\beta_\zeta^0|} + \frac{\kappa}{2}\left(\frac{\beta_\xi}{\beta_\xi^0} + \frac{\beta_\eta}{\beta_\eta^0} + \frac{\beta_\zeta}{\beta_\zeta^0} - 1\right)^2, \qquad (14)$$

$$\beta = -\beta_\eta + \beta_\xi \frac{1 + i\sqrt{3}}{2} + \beta_\zeta \frac{1 - i\sqrt{3}}{2},$$

which contains an integration constant κ to be considered later. The form (14) offers the special features that there are stationary points at the three corners of the triangle defined by the values $\{\beta_\xi^0\ 0\ 0\}$, $\{0\ \beta_\eta^0\ 0\}$, $\{0\ 0\ \beta_\xi^0\}$. It will generally be assumed that the constant values are negative, corresponding to an effective exchange, giving spin pairing in the relevant bonds. The first point will be a minimum when

$$\text{for } \{\beta_\xi^0\ 0\ 0\}, \quad \beta_\eta^0 + \beta_\zeta^0 > 2\beta_\xi^0 \Rightarrow \min \qquad (15)$$

with similar conditions applying for the two others. A reasonable choice would then be to mark the first and the third point as minima and the second one as a saddle point. It can be argued that the reactant situation corresponds to the case when there are no exchange integrals between the hydrogen orbital and the η- and ζ-orbitals while the remaining one equals β_ξ^0 so that the energy is

$$\varepsilon = \alpha - \frac{2|\beta_\xi^0|}{3} + \frac{|\beta_\eta^0|}{12} + \frac{|\beta_\zeta^0|}{12} = \left(\alpha + \frac{|\beta_\xi^0|}{12} + \frac{|\beta_\eta^0|}{12} + \frac{|\beta_\zeta^0|}{12}\right) - \frac{3|\beta_\xi^0|}{4} \qquad (16)$$

and a model energy surface is then established from the relative energies of the three chosen states. The relationship between the β-variables and the geometrical features remains to be determined.

Molecular conformations are associated with coordinate vectors specifying the nuclear positions at equilibria on the relevant electronic potential energy surface. It has proved useful to define the distance between two conformations through a translationally and rotationally invariant measure based on mass weighted variables and a hyperspherical picture.[16] Such distances are a quantification of the *principle of least motion* suggested by Rice and Teller[17] and offer a more direct geometrical picture of molecular reorganisation.[18] Calculations for the methylindene moieties by the GAMESS[19] system provide results[20] in general agreement with previous efforts (see Ref. 10). The resultant structures give a set of points in the space of conformations and, when the focus is on the possible reaction path, it is found that the two energy minima for 1-methylindene and 3-methylindene are separated by a distance of 0.453 Å and by 14.4 kJ mol^{-1} in favor of the latter. An intermediate conformation, where the proton is bound to the apical carbon in the five-membered ring, has an energy of 96.5 kJ mol^{-1} above the 1-methylindene in the absence of a catalyzing base. It has a distance of 0.403 Å from the reactant conformation and 0.283 Å from the product. The total energies of these conformations can be substantially improved by treatments including electron correlation but do reflect that a path from reactant to product via the intermediate requires a high and wide barrier to be overcome.

The reaction will have a shorter path length by going more directly between the end points and it should be influenced by the last contribution in the form (13). This should lead to an expression where the value $|\beta_\eta^0|$ should be replaced by larger one: $|\beta_\eta^\gamma|$. Equivalence is maintained, for $\kappa = 0$, when

$$\frac{2\beta_\eta^2}{4}\left(\frac{1}{|\beta_\eta^\gamma|} - \frac{1}{|\beta_\eta^0|}\right) = -\tfrac{1}{2}\{\sqrt{(\alpha_h - \alpha_b)^2 + 4\gamma_h^2} - \alpha_b + \alpha_h\} = -\frac{2\gamma_h^2}{\sqrt{(\alpha_h - \alpha_b)^2 + 4\gamma_h^2} + \alpha_b - \alpha_h} \qquad (17)$$

and there appears a near linear relationship between the effective exchange integral and the coupling to the orbital catalyst. No very satisfactory geometry has been derived for the transition conformation in the presence of the base and thus no distances can be ascertained.

The model above deserves yet another comment. A small effective exchange integral $|\beta_\eta^0|$ reflects that $(\xi\zeta)$ represents exchange between two non-neighboring orbitals and is small. The other term, (ηh), decreases in numerical value with the distance from the η-orbital. This happens when the base 'lifts' the proton but it is then compensated by the term in the form (17). No immediately recognized flaws afflict the model which is in accord with the London–Eyring–Polanyi approach. It accounts for the influence of electron correlation when bonds are broken and formed through the map on valence bond structures, which permits the interpretation of the significant parameters as effective orbital exchange integrals. The resulting energy surface depends on three variables rather than a single reaction coordinate.

Epilogue

Theoretical comments on two problem areas considered by Göran Bergson are presented in this essay and it should be clear that a lasting mark on my work has been set by him. Bergson's ability to choose 'clean' problems which permit both a qualitative and quantitative examination in terms of basic quantum chemical concepts is admirable and he has been a leading figure in getting experimental organic chemists to accept the value of theory for the interpretation as well as design of experiments. I cherish our friendship and occasional collaboration.

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