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BONDING AND NON-BONDING

S. STERNHELL



The Royal Society of New South Wales



Sever Sternhell

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SEVER STERNHELL 1930 -

Sever Sternhell was born on 30 May, 1930 at Lwow, Poland. He had 4 years of primary school education in pre-war Poland, then 7 years of no schooling at all during World War II and its immediate aftermath. He arrived in Australia in February 1947, and the only formal secondary education that he had was the year of 1947 at Newington College, Stanmore, NSW. He then proceeded to the University of Sydney in 1948, graduating B.Sc. (1st. Class Hons.) in 1952, and M.Sc. in 1953 working under the supervision of Professor A.J. Birch and Dr. F. Lions. During 1953-1955 he worked as a research chemist at Beetle-Elliott (Plastics) Ltd. (now Monsanto), then he went to the Division of Coal Research, Commonwealth Scientific and Industrial Research Organisation (CSIRO), as Research Officer. In September 1958 he was promoted to Principal Research Officer, and then he was awarded leave of absence to study at Imperial College, London under Professor D.H.R. Barton, FRS (later Nobel Laureate); his Ph.D. work was mainly on the constitution of the complex diterpenoid limonin, but he also developed the unusual transformation of hydrazones into vinyl iodides and / or geminal diiodides, a reaction now known as the Barton-Sternhell reaction. He completed the requirements for his Ph.D., D.I.C. degrees late in 1960, and then returned to the CSIRO Division of Coal Research, North Ryde, N.S.W. In 1964 he was appointed as Senior Lecturer in the Department of Organic Chemistry, University of Sydney where he was promoted to Reader in 1967 and to Professor of Organic Chemistry in 1977, which position he held until retirement in mid-1998 with the title Emeritus Professor. He was Head of the School of Chemistry in 1977-1978, and in 1986. During periods of leave he held Visiting Professorships at the University of Tennessee (1969), Eidg. Technische Hochschule, Zurich (1972), University of Arizona (1974), and Oxford University (1979).

Sev Sternhell has served on numerous scientific and educational committees, and on the editorial boards of Nuclear Magnetic Resonance Abstracts (1964-1976), "Magnetic Resonance in Chemistry" (Wiley), Magnetic Resonance Analysis, and "Methods in Stereochemical Analysis" (Verlag Chemie). He was a Member of the Chemistry Panel of the Australian Research Council 1988-1992, and its Chairman 1991-1992; he also served in other capacities for this Body.

Honours and Awards (Pre 2014)

- 1973 FRACI (Fellow of the Royal Australian Chemical Institute)
- 1992 FAA
- 1992 Liversidge Research Lecture, Royal Society of New South Wales
- 2001 Centenary Medal

Biographical Sources

1. Personal communication.
2. Field, L.D., 'Professor Sev Sternhell', *Aust. J. Chem.*, 1999, 52, 1001-1002.

Scientific Publications by S. Sternhell

Between 1954 and 1999 S. Sternhell had some 196 publications, including authorship/co-authorship of 3 books and 3 book chapters.

BONDING AND NON-BONDING*

S. STERNHELL

Department of Organic Chemistry, University of Sydney, N.S.W.

ABSTRACT. Over the last 10 years our group has carried out two parallel experimental investigations in physical-organic chemistry. The first one dealt with the development of a new experimental parameter for the determination of the π -bond order of the carbon-carbon double bond and the utilisation of this new parameter in the determination of the ground-state electronic structures of some unsaturated systems.

The second investigation dealt with the limitations of a previously proposed (Bott, Field and Sternhell, 1980) semi-quantitative treatment for predicting the severity (energy penalty) of repulsive non-bonded interactions from purely structural parameters.

The π -Bond Order of Carbon-Carbon Double Bonds

The notions of the π -bond order, or the mobile bond order, or indeed the σ - π description of the carbon-carbon double bond, are purely theoretical concepts although elementary text-books give them an air of experimental reality. An examination of the correlation of experimental variables, such as the carbon-carbon bond lengths (Pauling, 1980), vicinal interproton spin-spin coupling constants (Bartle, Jones and Matthews, 1969), and other NMR parameters (Marshall, 1983; Kalinowski, Berger and Braun, 1984; Joseph-Nathan, Garcia-Martinez and Morales-Rios, 1990) shows that they are, at best, semi-quantitative whichever calculated set of π -bond orders is chosen for the comparison.

We have developed (Barfield, Fallick, Hata, Sternhell and Westerman, 1983; Barfield, Collins, Gready, Sternhell and Tansey, 1989) a new NMR parameter, namely the 4-bond *orthobenzylic* interproton coupling constant involving a methyl group (henceforth referred to as ${}^4J_{\text{OB}}$) which shows excellent correlation with either the Pauling bond-order (Fig. 1) or the square of the SCF/MO bond-order as required by theory (Barfield, Fallick, Hata, Sternhell and Westerman, 1983; Barfield, Collins, Gready, Sternhell and Tansey, 1989). Moreover, the parameter ${}^4J_{\text{OB}}$ proved insensitive to other structural features such as ring-size and the presence of polar substituents or heteroatoms (Collins, Hatton, Sternhell and Tansey, 1987) within aromatic systems.

It now became possible to investigate by a purely experimental method the π -bond order in unsaturated systems of interest and hence to gain an insight into the ground-state distribution of π -electrons in them. We were thus able to demonstrate the following effects:

(i) According to our method, the Mills-Nixon Effect (ground-state bond fixation in tetralins, indanes etc.) does not exist (Collins, Gready, Sternhell and Tansey, 1990).

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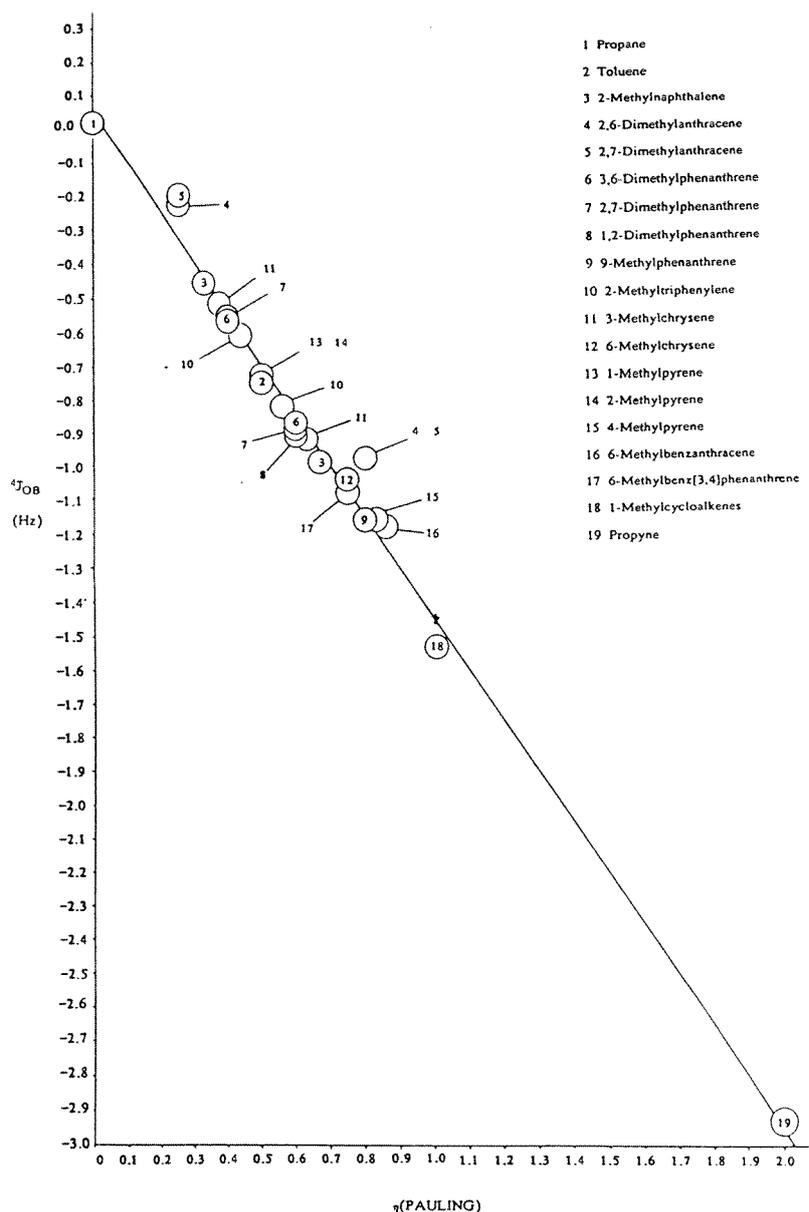


FIGURE 1. A plot of ${}^4J_{OB}$ against the Pauling bond order (η Pauling)

(ii) Our parameter shows very good correlation with SCF/MO bond-orders in a large variety of heteroaromatic systems (Gready, Hatton and Sternhell, 1992).

(iii) The presence of pairs of +R/-R substituents on a benzene ring in either the *para* or the *ortho* configuration causes significant ground-state bond-fixation (Collins, Hatton and Sternhell, 1992). The same effect can be observed in suitably substituted heteroaromatic systems (Collins, Hatton and Sternhell, 1992) and leads to a novel and completely independent method for the determination of Taft's δ^K substituent parameters (Hatton and Sternhell, 1993).

(iv) The electron distribution in free-base porphyrins (Crossley, Harding and Sternhell, 1992) corresponds to an [18]-annulene with the bond order between the β - β pyrrolic protons within the annulenic system approximately as high as the α - β bond in naphthalene. The β - β pyrrolic bonds *outside* the annulenic systems are essentially isolated double bonds.

(v) The ground-state π -electron distribution in azulene and biphenylene are as intuitively expected, i.e., azulene shows evidence of electron-transfer from the seven-membered ring towards the five-membered ring and biphenylene exhibits a radialene-like distribution (Collins, Sternhell and Tansey, 1990). More unexpectedly, the bond-orders in 1,6-methano-[10]annulene are in accord with intuition (i.e., the π -electron density in the α - β and the β - β bonds is the same), but *not* in accord with structural data (Collins, Sternhell and Tansey, 1990).

(vi) In a moderately distorted benzene (Hambley, Sternhell and Tansey, 1990) and phenanthrene (Sternhell and Tansey, 1990), as well as in a number of severely distorted *paracyclophanes* (Gready, Hambley, Kakiuchi, Kobiro, Sternhell, Tansey and Tobe, 1990) the π -bond orders appear to be normal, i.e., rehybridization occurs to maintain p-p overlap in spite of the distortions imposed on the δ -skeleton.

(vii) Finally, our method gave independent confirmation (Craw, Hush, Sternhell and Tansey, 1992) of the phenomenon of long-range perturbation of electron distribution in benzene rings by apparently isolated double bonds elsewhere in the molecule.

We consider the results summarised under (vi) to be the most interesting outcome of these investigations and they have led us to the wider question of the shape of the potential energy curve associated with the decoupling of the π -bond in ethylene during a pure rotational distortion of the δ -framework. We are at present engaged in the synthesis of appropriate molecules and the study of the rotational barriers in them.

Non-Bonded Interactions

Repulsive steric interactions ("steric hindrance") are simple conceptually ("two into one will not go"), but notoriously difficult to investigate in a quantitative manner. Some years ago (Bott, Field and Sternhell, 1980) we proposed a simple measure of severity of steric interactions which we named "apparent overlap". This amounts to measuring the overlap between van der Waals' surfaces involved in repulsive interactions as if the surfaces actually passed through each other, which is clearly not the case and hence the origin of the qualifying term "apparent". It transpired that for a variety of systems (Bott, Field and Sternhell, 1980) not only was the relationship between the height of the rotational barrier ("energy penalty") and apparent overlap linear, but the proportionality constants fell within a narrow range for different systems. Our original work (Bott, Field and Sternhell, 1980) was based mainly on biaryls but we have extended it to imides (Newsom, 1984), 9,10-dihydrophenanthrenes (Cosmo and Sternhell, 1987) and *meso*-tetraarylporphyrins (Crossley, Forster, Harding and Sternhell, 1987). We have also extended this study to the relationship between static deformation (Cosmo, Hambley and Sternhell, 1987) and apparent overlap and found surprisingly good correlations.

However, not unexpectedly there proved to be no correlation between apparent overlaps and the equilibrium internuclear distances of the repulsively interacting nuclei emphasising the artificiality of the concept of "apparent overlap". An unexpected, indeed highly counter-intuitive result, was that in a number of cases (Cosmo, Hambley and Sternhell, 1987) the same pairs of nuclei (in particular halogens) proved to be closer (crystallographic results) for cases (1,8-disubstituted naphthalenes) where the δ -framework would predict them to be further than in other cases (4,5-disubstituted phenanthrenes). This anomaly could have two explanations (Cosmo, Hambley and Sternhell, 1987), viz.,

that either the *angle of approach* was critical for the 'distortibility' of the van der Waals' surfaces or that the partitioning (Allinger, 1976) of the repulsive energy between the distortion of the van der Waals' surfaces and skeletal distortion caused the "stiffer" naphthalene nucleus to squeeze the halogens in the 1,8-juxtaposition more than the apparently "closer" halogens in the 4,5-juxtaposition of phenanthrenes.

The synthesis of a number of compounds designed to discriminate between these two hypotheses was undertaken and crystallographic data for a total of 11 new highly crowded compounds were obtained. From these results (Hambley and Sternhell, 1992) it was possible to conclude that it was the second of the rival hypotheses that is correct. As an interesting by-product of this investigation, we have collected our own and literature data for the closest intramolecular distances between pairs of atoms, viz., -H, -F, -OMe, -Cl, -SMe, -Br and -I ever reported. While it will never be possible to claim that any such set of data are "the most crowded *possible* cases", two remarkable correlations can be drawn from our data.

(i) The apparently maximum compressions possible appear to be remarkably similar for the above atoms, ranging between 0.45 and 0.72 Angstrom, suggesting that these elements have similar compressible outer layers.

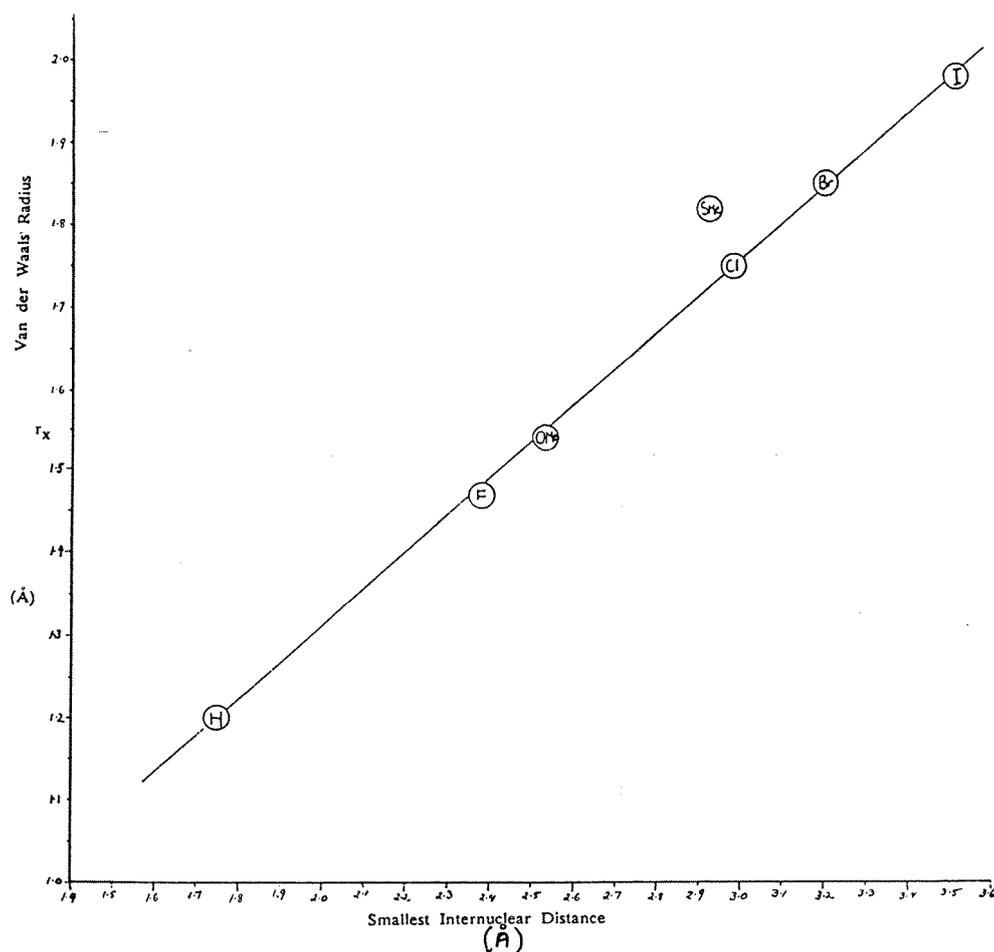


FIGURE 2. Plot of Van der Waals' radius against closest internuclear distance for each substituent

(ii) A plot of the "record" minimum distances from our crystallographic data (Hambley and Sternhell, 1992) (Fig.2) against the van der Waals' radii of the atoms involved is a straight line.

These phenomena are being further investigated by the design, synthesis and crystallographic studies of further crowded compounds.

Acknowledgements

I wish to acknowledge the fruitful collaboration with my colleagues Drs M.J. Crossley, L.D. Field, T.W. Hambley and M.M. Harding and Prof. N.S. Hush, as well as of the numerous Postgraduate and Honours students listed in the publications. Both phases of this research were supported by the Australian Research Council.

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Photograph taken on the occasion of the 28th Liversidge Research Lecture 1992, Royal Society of New South Wales:

Left to right (clockwise): Dr. F.L. Sutherland (President of the Society 1992/93), Prof. Sev Sternhell (Liversidge Lecturer 1992), Prof. Noel Hush (School of Chemistry, University of Sydney), Prof. Bob Gilbert (School of Chemistry, University of Sydney), Dr. Peter Lay (Secretary of the Chemical Society), Dr. Tony Masters (President of the Chemical society), Prof. Hans Freeman (21st Liversidge Lecturer 1978; School of Chemistry, University of Sydney).

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