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Selective INADEQUATE, a Farewell to 2D-NMR?*

By Stefan Berger*

The INADEQUATE pulse sequence,^[1] especially the two-dimensional (2D) variant,^[2] is one of the most important ^{13}C -NMR methods for determining the structure of organic substances.^[3] When all other modern NMR methods are of no further help, decisively important information can often be obtained with 2D-INADEQUATE. Prerequisite is a sufficient concentration of ^{13}C -disubstituted molecules, since typically 128 ^{13}C -NMR spectra must be recorded for a complete data matrix. The digital resolution in ω_2 is limited in the case of 2D-methods and makes the evaluation of C,C coupling constants over more than one bond from 2D-INADEQUATE NMR spectra^[4,5] difficult.

There has been no lack of attempts in recent years to make INADEQUATE more sensitive,^[6-8] but none of the improvements put forward so far can be considered as of general utility. Kessler^[9] and Freeman^[10] have recently indicated how 2D-methods by *frequency-selective excitation* can be reduced to the recording of a few 1D-NMR spectra. Some 2D-INADEQUATE experiments of limited application have also been reported.^[11-13] In continuation of our INADEQUATE studies^[4,5,14,15] we present here a gener-

al coherence of those carbon nuclei is transferred to observable magnetization for which the frequency of the frequency-selective pulse is adjusted. We have also found that the bandwidth of the frequency-selective pulse must correspond to the C,C-coupling constant. All pulse phases remain the same as described for the original experiment,^[3] but the phase of the frequency-selective pulse must be correctly adjusted in relation to the phases of the non-selective pulses as well as to the receiver phase. All known variants of the 1D-INADEQUATE experiment can also be applied to the pulse sequence in Figure 1.

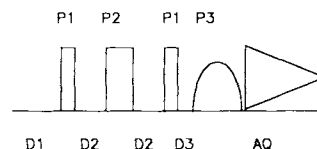


Fig. 1. Pulse sequence for SELINQUATE. D1 relaxation delay, D2 focussing delay $1/4 J_{\text{C,C}}$, D3 transfer delay, P1, P2 non-selective pulses 90° and 180° , AQ acquisition time. Exact recording conditions, see [16].

The result of the pulse sequence of Figure 1 is shown in Figure 2, for the sake of simplicity in the case of *n*-propanol as example.^[16] Trace (a) shows the normal ^{13}C -NMR

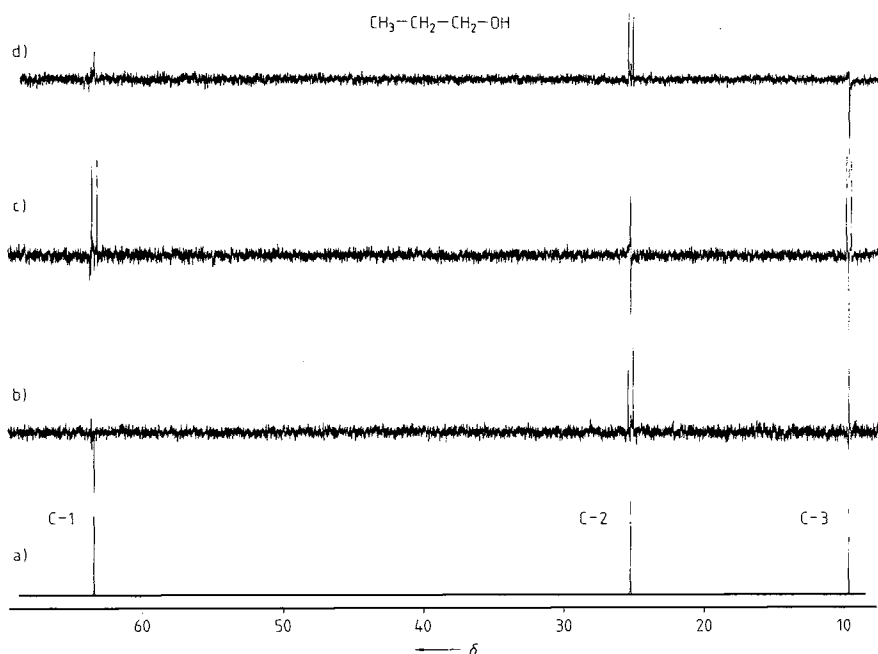


Fig. 2. ^{13}C -NMR spectra of *n*-propanol. (a) Standard ^{13}C -NMR spectrum, (b-d), Recording after pulse sequence in Fig. 1, (b) P3 adjusted to signal of C-3, (c) P3 adjusted to signal of C-2, (d) P3 adjusted to signal of C-1.

ally applicable frequency-selective version of INADEQUATE which makes 2D-recordings superfluous.

Figure 1 shows the pulse sequence "SELINQUATE" in which the fourth pulse of the standard INADEQUATE sequence is replaced by a frequency-selective pulse. It is therefore not a frequency-selective excitation, but a frequency-selective transfer of coherence. Only double quan-

spectrum. In traces (b-d) the frequency-selective pulse was in each case adjusted to C-3, C-2 and C-1; accordingly, in (b) only the doublet of C-2 which couples with C-3 (36.1 Hz) is observable, in (c) the doublets of C-1 and C-3 which couple with C-2 (36.1 and 34.2 Hz), and in (d) the doublet of C-2 which couples with C-1 (34.2 Hz).

In order to obtain complete information of the coupling of all C atoms in a molecule only the recording of the ^{13}C -NMR spectra of exactly the number of differentiable carbon atoms present is necessary; moreover, this can be done with high digital resolution, so that all coupling constants can be correctly measured. The determination of

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the structure of organic compounds is thus considerably simplified,^[17] and all the more so in practice, since seldom are all C,C couplings needed but only must be proven for a few C atoms.

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BOOK REVIEWS

Organic Chemistry: The Name Game. Modern Coined Terms and Their Origins. By A. Nickon and E. F. Silversmith. Pergamon Press, Oxford 1987. xii, 347 pp., bound, £ 45.00.—ISBN 0-08-035157-3; paperback, £ 18.00.—ISBN 0-08-034481-X

Named reactions are a time honored and useful feature of chemical literature and communication; the custom of *name-dropping* is at least equally old, even though it usually fails to produce the intended effect. But a *name game*?—or, more exactly, “Organic Chemistry: The Name Game”, to give the recently published monograph by Alex Nickon and Ernest F. Silversmith its full title. Can the serious and sober discipline of organic chemistry be a game with words? This, and much more besides, is the theme of “The Name Game”. The book, generously illustrated with excellent structural formulas, reaction schemes and other diagrams, is in the first place a collection of modern trivial names and accounts of how they originated. Developed out of a student project aimed at discovering the origins of a wide variety of expressions, the authors have based the compendium not only on an intensive study of the literature, but also on innumerable personal contacts over a period of about ten years. To limit the size of the compilation, the naming of natural products, and commercial product and brand names, are dealt with only briefly; the result is not a comprehensive index of trivial names, but instead a real book, for both serious reading and browsing. And no matter where one dips into it, fascination quickly takes hold, and one becomes absorbed in reading. To appreciate this even more fully, imagine for a moment the effect if a work of a similar kind had instead been produced in an (admittedly more comprehensive) “electronic version”!

What, then, are the origins of the names given to the many organic compounds prepared for the first time during recent years, and to newly discovered reactions? Who or what agency first coined these names, what prompted

this, and what are their etymologies? Answer: the names are as varied as are the people involved in chemistry, and they reflect the personal qualities and idiosyncracies of their creators: their sense of humor (or lack of it), their vanities, their education (or its shortcomings), their knowledge of the world, or their provincialism. Nevertheless, as the authors show in the 20 chapters and six appendices of the book, it is possible to recognize certain common features and families of words and names, which together illustrate the rather childlike pleasure that chemists take in naming the objects resulting from their work. There is an abundance of names of animals; articles of apparel—especially head coverings—provide inspiration; names that clearly have their origins in children’s toys, and which grown-ups (?) now have, are widespread, some of the most popular being building bricks, water-wheels and airplanes. Foodstuffs play a role to some extent. Above all, containers of every kind have a great fascination—objects into which things can be put. In due course we leave the household behind, and travel through cities and across national frontiers, even as far as the stars. In short, nothing escapes being used to form names, and inexorably there comes into being at the molecular level a more and more fully equipped micro-universe.

Furthermore, “The Name Game” shows that the number of trivial names has grown alarmingly just in recent times (and consequently the book is also very useful as a dictionary, despite the limitation on size mentioned earlier). One possible cause for this is that the standard language, i.e. the IUPAC nomenclature rules, cannot keep pace with the complexity of the structures which have been analyzed and/or synthesized. Another factor is the notorious inadequacy of this nomenclature system for describing the dynamics of chemical reactions. New developments are essential here if we are to avoid becoming completely entangled in our own special jargon. It is conceivable, for example, that for “supermolecules” (cage structures of all kinds, layered molecules) a method of nomen-