Summary

Nuclear magnetic resonance (NMR) deals with isotopes possessing a nuclear magnetic dipole moment. The nuclei are used as probes to explore the internal magnetic fields in solids. Thus NMR has become a new tool in solid-state physics. Some typical examples of the application of NMR to solid-state problems are discussed.

The location and orientation of water molecules in crystals are determined by NMR with relative ease. The second moment of an NMR line shape yields information on the structure as well as on the mobility of the atoms. The various types of resonance frequency shifts may be used for the understanding of the interactions and bonds in the solid and the dynamics of the crystal lattice.

Very important are nuclei possessing both a magnetic dipole and an electric quadrupole moment. They serve as very sensitive detectors of the internal electric fields prevailing in solids. Apart from further structural information, NMR spectra influenced by electric quadrupole interaction may be used for studying such topics as aluminium-silicon ordering in feldspars or phase transitions in ferroelectrics.

The utility of NMR in treating problems of the bonding is exemplified by showing that the covalent effects in the alkali halides are very small.

Some investigations of ferromagnetism, antiferromagnetism and superconductivity are mentioned.

SPECIALIA

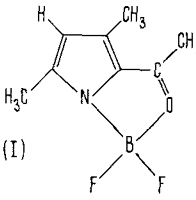
Acetyl Pyrroles and Boron Trifluoride Adducts

Acetoacetyl pyrroles react with $BF_3 . Et_2O$ to give the 6 member chelate. The identity of these products has been established by infrared, nuclear magnetic resonance and degradative studies[1]. In the present communication the reaction of acetyl and benzoyl pyrroles with $BF_3 . Et_2O$ have been studied in order to check if similar boron complexes are formed with the nitrogen of the pyrrole to form 5 member chelate[2,3].

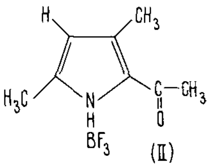
2,4-Dimethyl 5-acetyl pyrrole[4] on treatment with $BF_3 . Et_2O$ in benzene gave a compound which was crystallized from ether/petroleum ether, mp 146–148°. The IR-spectra showed absorption in the regions 3334 cm^{-1} and 1640 cm^{-1} which are attributed to N–H and C=O stretching frequencies. The nuclear magnetic resonance spectra showed signals at 2.25, 2.36, 2.4 (singlets, $-COCH_3$, β- and α-CH_3), 5.8 (doublet, β-H, probably due to the coupling with the N–H proton) and 9.75 ppm (broad, N–H) in relative intensities 3:3:3:1:1. The ^{19}F nuclear magnetic resonance spectrum was also recorded. The ^{19}F chemical shift with CF_3COOH as external reference and B–F coupling constant for this compound are:

$$\delta_{BF_3} = 4074.5 \text{ cps.}$$
$$J_{B\text{-}F} = 2.4 \text{ cps.}$$

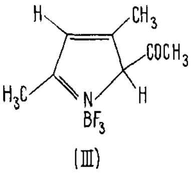
There may be little error in the measurement of B–F coupling constant due to the quadrupole broadening in ^{19}F spectrum. ^{19}F chemical shift of BF_3 group in other compounds have been reported elsewhere[5,6]. The elemental analysis are as follows: found C,47.32; H, 6.01; N, 7.17. Molecular weight was found to be 210.8. Heating with dilute alkali gave the parent compound. Comparison of this with the original compound which has bands at 3320 cm^{-1} N–H and 1630 cm^{-1} C=O in IR-spectra, the nuclear magnetic resonance spectra exhibit signals at 2.25, 2.3, 2.4 (singlets 3H each, $-COCH_3$, β- and α-CH_3),



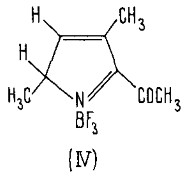
(I)



(II)



(III)



(IV)

---

[1] M. W. Roomi, Can. J. Chem. *47*, 1099 (1969).

[2] K. Niedenzu and J. W. Bawson, *Boron-Nitrogen Compounds* (Academic Press Inc., New York 1965).

[3] H. Steinberg, *Organoboron Chemistry* (John Wiley and Sons Inc., New York 1964), vol. 1. – H. Steinberg and R. J. Brotherton, *Boron-Nitrogen and Boron-Phosphorus Compounds* (John Wiley and Sons Inc., New York 1965), vol. 2.

[4] H. Fischer and H. Orth, *Die Chemie des Pyrrols* (Akademischer Verlag, Leipzig 1934), vol. 1, p. 186.

[5] T. D. Coyle, S. L. Stafford and F. G. A. Stone, J. chem. Soc. (*1961*), 3103.

[6] T. C. Farrar and T. D. Coyle, J. chem. Phys. *41*, 2612 (1964).

5.8 (doublets, 1H, β-H) and 9.6 ppm (broad, 1H, N–H), showed that the compound formed was not the 5 member chelate (I) but an adduct (II) (Anal. calcd. for $C_8H_{11}NOBF_3$, 204.97, C, 46.90; H, 5.41; N, 6.84). Pyrrolenine structures (III) and (IV) are also possible for the above compound but have been ruled out by IR-analysis (N–H stretching frequency around 3300 cm^{-1}) and by nuclear magnetic resonance which showed only 1 ring proton instead of 2 as expected from (III) and (IV). The 2-acetyl and 2, 4-dimethyl 5-benzoyl pyrroles on similar treatment with $BF_3.Et_2O$ gave hygroscopic adducts which on exposure to air gave the parent compounds[7].

Zusammenfassung. Es wird gezeigt, dass bei der Reaktion von 2-Acetylpyrrol mit $BF_3.Et_2O$ das Addukt (II) entsteht und nicht wie erwartet der Fünferring des Chelats (I).

M. W. ROOMI[8]

Organisch-Chemisches Institut der
Technischen Hochschule,
München (West Germany), 11 August 1969.

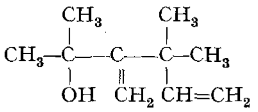
---

[7] Acknowledgements. The author is grateful to Professor A. TREIBS for his advice and encouragement during the course of this work and Alexander-von-Humboldt-Stiftung for the award of the Fellowship.

[8] Present address: Biochemistry Laboratory, National Research Council of Canada, Ottawa (Canada).

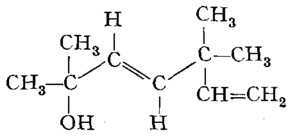
Revised Structure of Yomogi Alcohol A from *Artemisia feddei* Lév. et Van.

In a recent report[1], formula I was proposed for yomogi alcohol A, a monoterpene isolated from the essential oil of *Artemisia feddei* Lév. et Van. Re-examination of the original data, plus results of further experiments, reveals that the structure of yomogi alcohol A should be revised to II, an allylic rearrangement product of β-artemisia alcohol III[2].

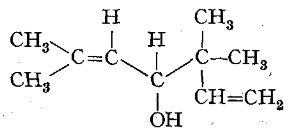


$$\mathrm{CH_3{-}\underset{OH}{\overset{CH_3}{C}}{-}\underset{CH_2}{\underset{\|}{C}}{-}\underset{CH{=}CH_2}{\overset{CH_3}{C}}{-}CH_3}$$

I



II



III

Previously, a 2-proton singlet at 5.60 ppm in the NMR-spectrum of yomogi alcohol A was assigned to a vinylidene group[1]. However, the proton signals of a non-conjugated vinylidene function normally appear at higher field in the region 4.6–4.7 ppm[3]. Moreover, a strong C–H bending vibration at 975 cm^{-1} in the IR-spectrum, in addition to the corresponding vinyl absorptions at 995 and 910 cm^{-1}, points to the presence of a *trans*-disubstituted ethylenic bond, in agreement with structure II but not I.

On selective hydrogenation over Adams platinum oxide in methanol, yomogi alcohol A, like III[2], consumed 1 mole of hydrogen. The IR-spectrum of the product lacked the characteristic vinyl absorptions of the starting material[1] but retained the strong band at 975 cm^{-1}. The signals of the ABX pattern of the vinyl group in the starting material[1] were absent in the NMR-spectrum, and only a single 2-proton peak at 5.77 ppm was present in the olefinic region. The dihydro alcohol consumed an additional molar equivalent of hydrogen with Adams platinum oxide in acetic acid[2] giving a product that no longer had either the IR-band at 975 cm^{-1} or the olefinic proton NMR-signal at 5.77 ppm.

These data indicate that the unsplit signal at 5.60 ppm in the NMR-spectrum of yomogi alcohol A is due to the protons of a *trans*-1, 2-disubstituted ethylene bonded to 2 nearly equivalent quaternary carbon atoms. Thus yomogi alcohol A is *trans*-2, 5, 5-trimethyl-3, 6-heptadien-2-ol II, and the disubstituted butadiene (λ_{max}^{EtOH} 229 nm, log ε 4.40) formed by mild dehydration[1] is undoubtedly the same 2, 5, 5-trimethyl-1, 3, 6-heptatriene (λ_{max}^{EtOH} 229 nm, log ε 4.39) obtained previously from III by TAKEMOTO and NAKAJIMA[2].

Other constituents of the essential oil of *Artemisia feddei* Lév. et Van. have been investigated, and compounds of the artemisia keton type (cf. III) were found to comprise about 60% of the oil. Hence the formulation of yomogi alcohol A as II is also favoured on biogenetic grounds[4].

Zusammenfassung. Für den aus dem ätherischen Öl von *Artemisia feddei* Lév. et Van isolierten Yomogialkohol A wird die neue Struktur des *trans*-2, 5, 5-Trimethyl-3, 6-heptadien-2-ols vorgeschlagen.

K. YANO[5], S. HAYASHI[6],
T. MATSUURA[6] and A. W. BURGSTAHLER[7]

Department of Chemistry,
Fukuoka University of Education,
Munakata-machi, Munakata-gun,
Fukuoka (Japan), 15 July 1969.

---

[1] S. HAYASHI, K. YANO and T. MATSUURA, *Tetrahedron Letters 6241* (1968).

[2] T. TAKAMOTO and T. NAKAJIMA, J. pharm. Soc. Japan *77*, 1310 (1957).

[3] Cf. olefinic proton chemical shifts of 4.61–4.65 ppm recorded for 2-alkyl-1-alkenes in the Sadtler NMR-Spectra Catalogue.

[4] R. B. BATES and S. K. PAKNIKAR, *Tetrahedron Letters 1453* (1965).

[5] We are grateful to Professor TAKU MATSUO of Kyushu University for the NMR-spectra.

[6] Department of Chemistry, Faculty of Science, Hiroshima (Japan).

[7] Department of Chemistry, The University of Kansas, Lawrence (Kansas 66044, USA).