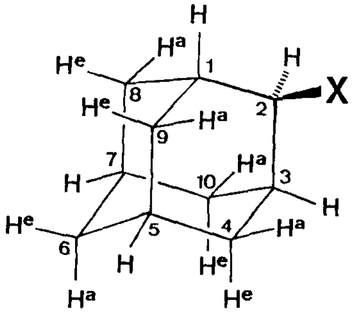
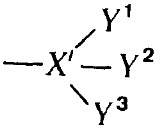
Tetrahedron Letters, Vol.27, No.4, pp 473-476, 1986 0040-4039/86 $3.00 + .00
Printed in Great Britain

SEQUENCE OF δ-CARBON SIGNALS IN 2-SUBSTITUTED ADAMANTANES DETERMINED BY TWO-DIMENSIONAL CORRELATED NMR SPECTROSCOPY

Helmut Duddeck*, Manfred Kaiser[1] and Doris Rosenbaum
Ruhr-Universität Bochum, Fakultät für Chemie,
D-4630 Bochum 1, BRD

Abstract: The δ-carbon resonances of 23 2-substituted adamantanes were assigned unequivocally by two-dimensional (2D) correlated NMR spectroscopy. It is shown that in contrast to all previously published instances the δ carbon signal sequence is reversed for 10 other substituents.





Since the advent of one- and two-dimensional double-quantum ^{13}C NMR spectroscopy (INADEQUATE)[2] new interest arose in the signal assignments of substituted adamantanes[3-6] and diamantanes[4,7]. Very recently, our previous assignments in some 2-substituted adamantanes[8] were confirmed by 2D-INADEQUATE experiments[5] for X=Br and C_6H_5. Thus, one may be led to the conclusion that, apparently in general, the C^7 atom (δ-anti) is more shielded that C^5 (δ-syn). However, our latest highfield ^1H and ^{13}C NMR investigation of these compounds showed that this is not at all correct. Therefore, we want to present preliminarily our results concerning the sequence of the δ-carbon signals.

Our unequivocal assignment is based on a combination of hetero- and homonuclear correlated 2D NMR spectroscopy[10]. This is demonstrated for X = $C(CH_3)_2OH$ in Figs. 1 and 2: the H^4/H^9 and H^8/H^{10} signals can be identified by the heteronuclear (^1H-^{13}C) correlated 2D NMR spectrum

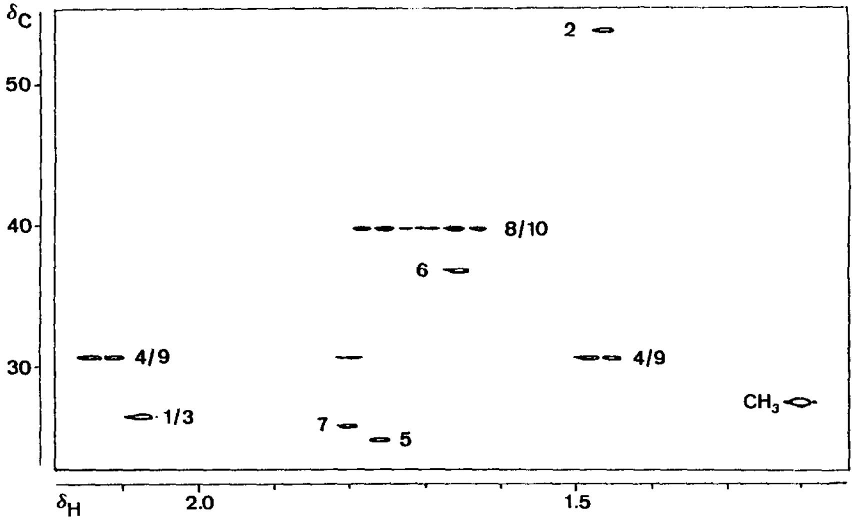


Fig.1: ^{1}H-^{13}C correlated 2D NMR spectrum of (2-adamantyl)dimethylcarbinol, X = $C(CH_3)_2OH$

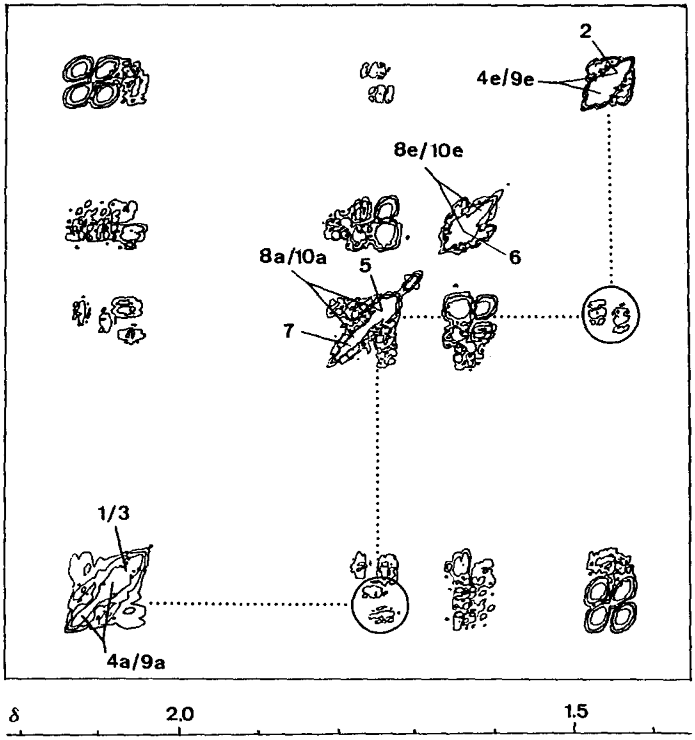


Fig.2: ^{1}H-^{1}H correlated 2D NMR spectrum of (2-adamantyl)dimethylcarbinol, X = $C(CH_3)_2OH$

Table 1: Differences Δδ between H^5/H^7 and C^5/C^7 resonances in 2-substituted adamantanes[a,b]

	Δδ			Δδ	
X	^1H	^{13}C	X	^1H	^{13}C
CH_3	-0.09	+0.4	$N(CH_3)_3^+\ I^-$	+0.06	-1.0
2-adamantyl	+0.15	+0.3	$PO(OCH_3)_2$	-0.03	-0.6
$C(CH_3)_3$	-0.03	-1.0	OH	-0.01	+0.5
$C(CH_3)_2OH$	-0.06	-0.9	$OCOCH_3$	-0.01	+0.2
$C_4H_7S_2$	-0.04	-0.4	OSO_2CH_3	+0.01	+0.3
COOH	-0.07	0	SH	-0.01	+0.8
CN	+0.02	+0.2	SC_2H_5	-0.01	+0.4
$Si(CH_3)_3$	-0.06	-0.7	SOC_2H_5	+0.02	-1.6
$Ge(CH_3)_3$	-0.05	-0.5	$SO_2C_2H_5$	+0.02	-0.8
$Sn(CH_3)_3$	-0.03	-0.4	F[c]	0	+0.3
NH_2	-0.03	+0.4	Cl[c]	0	+0.6
$N(CH_3)_2$	-0.03	+0.2	Br[c]	0	+0.6
$NH(CH_3)_2^+\ Cl^-$	+0.03	+0.1	I	-0.08	+0.6

[a] Δδ = δ(5) - δ(7); cf. formula scheme.

[b] Bruker AM-400 spectrometer; 400 MHz (^1H) and 100.6 (^{13}C); 5-mm dual-probehead; solvent $CDCl_3$ except for the ammonium salts (CD_3OD).

[c] Assignments taken from refs. 4, 5 and 8.

(Fig.1) since the sequence of the corresponding carbon signals is determined by the γ-gauche effect of X upon C^4/C^9. Then the proton connectivity is established by a ^1H-^1H correlated spectrum (COSY45, Fig.2). For the well separated signals of H^{4a}/H^{9a} and H^{4e}/H^{9e} cross-peaks (encircled) exist only for one of the hydrogens at the δ-carbon atoms. Thus, this must be H^5 whereas the other is H^7. Finally, the heteronuclear correlated spectrum allows the unambiguous C^5/C^7 assignment as well.

This method is complementary to the elegant ab-initio carbon connectivity determination by 2D-INADEQUATE measurements[2,5] which, however, are hampered by two severe drawbacks: they are time-consuming and require large quantities of material which may not always be available. The two measurements described here can be performed in less than four hours with about 50-100 mg.

An inspection of the data collected in Table 1 shows that $\Delta\delta(^{13}C) = \delta(C^5) - \delta(C^7)$ is positive for 15 derivatives and among these are all published by us previously[8]. For 10 of them, however, $\Delta\delta(^{13}C)$ is negative, and it is striking that all substituents $X'Y^1Y^2Y^3$ with $Y^i \neq O$ (cf. formula scheme) belong to this latter group[11]. The decreasing absolute values in the sequence $X=M(CH_3)_3$ ($M=N^+$,C,Si,Ge,Sn) seem to suggest that steric congestion might be involved. It is, however, not readily understandable why $\Delta\delta\ (^{13}C)$ for X = 2-adamantyl is positive, but negative for 2-(1',3'-dithianyl) ($C_4H_7S_2$). Even more surprising are the marked differences between the $\Delta\delta(^{13}C)$-values of the various sulfur functions and the two ammonium halides. The latter indicates that apparently polar through-space effects do not play a dominant role in δ-carbon substituent effects. Finally, it should be noted that the sign variations of $\Delta\delta(^{13}C)$ are not paralleled by corresponding differences Δδ (^1H) of the H^5/H^7 signals.

It must be concluded that the mechanisms governing the δ carbon substituent effects in such configurations are not yet understood so that assignments based on mere analogy arguments should be strongly discouraged. Only unambiguous assignments like those from 2D NMR measurements[5,9] or selective deuteration[6] are safe.

REFERENCES

[1] Present address: BICT, Großes Cent, D-5351 Swisttal-Heimerzheim, BRD.

[2] A. Bax, R. Freeman and S. Kempsell, J. Am. Chem. Soc. **102**, 4849 (1980); J. Magn. Reson. **41**, 349 (1980); A. Bax and R. Freeman, J. Magn. Reson. **41**, 507 (1980); A. Bax , R. Freeman and T.A. Frenkiel, J. Am. Chem. Soc. **103**, 2102 (1981); T.H. Mareci and R. Freeman, J. Magn. Reson. **48**, 158 (1982); A. Bax and T.H. Mareci, J. Magn. Reson. **53**, 360 (1983).

[3] V.V. Krishnamurthy, P.S. Iyer and G.A. Olah, J. Org. Chem. **48**, 3373 (1983).

[4] G.A. Olah, J.G. Shih, V.V. Krishnamurthy and B.P. Singh, J. Am. Chem. Soc. **106**, 4492 (1984).

[5] A.N. Abdel-Sayed and L. Bauer, Tetrahedron Lett. **26**, 2841 (1985).

[6] An assignment of the δ carbon signals of 2-adamantanol by selective deuteration is also noteworthy: S. Srivastava, C.K. Cheung and W.J. le Noble, Magn. Reson. Chem. **23**, 232 (1985).

[7] V.V. Krishnamurthy, J.G. Shih and G.A. Olah, J. Org. Chem. **50**, 1161 (1985).

[8] H. Duddeck, Org. Magn. Reson. **7**, 151 (1975); H. Duddeck and W. Dietrich, Tetrahedron Lett. **1975**, 2925; R. Gerhards, W. Dietrich, G. Bergmann and H. Duddeck, J. Magn. Reson. **36**, 189 (1979); H. Duddeck and M.R. Islam, Org. Magn. Reson. **21**, 140 (1983).

[9] H. Duddeck, M. Kaiser and D. Rosenbaum, in preparation.

[10] A. Bax, "Two-Dimensional Nuclear Magnetic Resonance in Liquids", Reidel, Dordrecht, 1982; R. Benn and H. Günther, Angew. Chem. **95**, 381 (1983), Angew. Chem., Int. Ed. Engl. **22**, 390 (1983).

[11] This is also valid for isomeric diadamantylphosphinic acid chlorides: H. Duddeck, M.H.A. Elgamal, A.G. Hanna and M. Kaiser, Tetrahedron **41**, 3763 (1985).

Acknowledgement

The authors gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

(Received in Germany 11 September 1985)