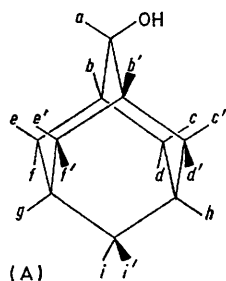


Configurations of the 5-Methyladamantan-2-ols and the 2,5-Dimethyladamantan-2-ols

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The configurations of the two secondary and the two tertiary alcohols whose synthesis is described in the preceding paper have been established unambiguously by analysis of n.m.r. spectra. Four techniques were used: (i) treatment of chemical shifts by the additivity relationship; (ii) study of degree to fit to the relationship between europium-induced shift and intramolecular distance; (iii) comparison between sensitivities of shifts to europium concentration; and (iv) investigation of the behaviour of the previously assigned protons of adamantan-2-ol, and spin decoupling in the europium-expanded spectrum. All results led to the same conclusions, and justify interchange of the configurations previously assigned to the secondary alcohols. The reliability of these methods is assessed.

In the preceding paper we describe the synthesis of a pair of secondary alcohols, the 5-methyladamantan-2-ols (A; $a = \text{H}$, g or $h = \text{Me}$) and a pair of tertiary alcohols, the 2,5-dimethyladamantan-2-ols [A; a and (g or h) = Me]. These were designated (Ia), (Ib), (IIa), and (IIb); to assign the relative configurations proved to be difficult.



We first utilise the n.m.r. shift additivity relationships of Fort and Schleyer for 1-substituted adamantanes,¹ with the assignments of van Deursen and Korver for 2-substituted adamantanes.² The shift additivity relationships were described for solutions in carbon tetrachloride, but control experiments with adamantane, 1-methyladamantane, adamantan-1-ol, and 3-methyladamantan-1-ol showed that they are equally applicable to solutions in pyridine, a better solvent for the alcohols which, moreover, gives a wider spread of chemical shifts, much more so than benzene.³ All spectra predicted for the two secondary and two tertiary isomers were obtained by applying the Fort-Schleyer shifts¹ and the van Deursen and Korver assignments² to the values actually found for adamantan-2-ol and 2-methyladamantan-2-ol in pyridine. Data for each of the two isomers, a and b, were compared with the two predicted spectra, for *cis*- and *trans*-isomers (referring to the 2-hydroxy and 5-methyl groups), in the secondary and tertiary cases (Tables 1 and 2); if we ignore proton *a* on the plane of symmetry running through the hydroxy, methyl, and hydrogen groups in question, the equivalent pairs bb' and ii' , and (in the secondary isomers) the groups g and h , we have four

different pairs of protons, cc' , dd' , ee' , and ff' , for which different predictions follow from different assumed configurations, and, in the tertiary alcohols, also protons g and h . For the secondary and tertiary cases, there are thus eight and ten sets of errors for either assumption ($a = \text{cis}$, $b = \text{trans}$; or $a = \text{trans}$, $b = \text{cis}$). In both cases, the first of these two assumptions gave an accumulated arithmetic error less than one quarter as large as the second. We can thus deduce that in the two a-isomers the hydroxy and methyl groups are *cis*, and in the two b-isomers these two groups are *trans*.

Unfortunately, in the secondary case, this assignment is contrary to two other pieces of evidence already published.⁴ The tertiary methyl signals should be subject to long-range deshielding from the hydroxy-group in the *cis*-, but not in the *trans*-isomer, if effects observed in 5 β -steroids⁵ and *cis*-decalols⁶ apply here. Although the shifts are minute (0.02 p.p.m.), they are certainly real, but they do not (as in the examples cited¹) increase with the use of pyridine as solvent; this throws some doubt on the assignment resulting from their use.

When derivatives of the secondary alcohols are solvolyzed in a variety of solvents, the configurations of the products are determined in part by that of the leaving group, but there is also a marked effect favouring attack of nucleophile from one side of the molecule. On the basis of the previous assignment, based on long-range deshielding of the 5-methyl group,⁴ this implied a preference for attack from the less encumbered side; the present assignment implies preferred attack on the cationic centre from the side bearing a methyl group (albeit at a distance unlikely to involve steric hindrance); this seemed surprising.

Because these two lines of argument conflicted with the foregoing assignments from chemical shifts, it seemed necessary to find deciding arguments. [Adherence to our earlier assignment⁴ would presumably necessitate some revision of the intricate arguments assigning the spectra of the unmethylated model compounds, adamantan-2-ol and 2-methyladamantan-2-ol,² and would leave unchanged the evidence, deduced

⁴ J. A. Bone and M. C. Whiting, *Chem. Comm.*, 1970, 115.

⁵ N. S. Bhacca and D. H. Williams, 'Applications of N.M.R. Spectroscopy in Organic Chemistry,' Holden-Day, San Francisco, 1964, p. 20.

⁶ J. I. Musher, *J. Amer. Chem. Soc.*, 1961, **83**, 1146.

¹ R. C. Fort and P. von R. Schleyer, *J. Org. Chem.*, 1965, **30**, 789.

² F. W. van Deursen and P. K. Korver, *Tetrahedron Letters*, 1967, **3923**.

³ J. W. Greidanus, *Canad. J. Chem.*, 1970, **48**, 3593.

TABLE 1
100 MHz Spectra of the secondary alcohols in pyridine (τ values ^a)

| Protons | Adamantan-2-ol | Predicted <i>cis</i> | Predicted <i>trans</i> | (Ia) | Δ <i>cis</i> (p.p.m.) | Δ <i>trans</i> (p.p.m.) | (Ib) | Δ <i>cis</i> (p.p.m.) | Δ <i>trans</i> (p.p.m.) |
|---------------------------|-------------------|----------------------|------------------------|------|---------------------------------|-----------------------------------|------|---------------------------------|-----------------------------------|
| <i>a</i> | 5.95 | 6.05 | 6.05 | 5.99 | | | 5.96 | | |
| <i>bb'</i> | 7.94 | 7.90 | 7.90 | 7.84 | | | 7.91 | | |
| <i>cc'</i> | 7.50 | 7.80 | 7.60 | 7.74 | -0.06 | +0.14 | 7.52 | -0.28 | -0.08 |
| <i>dd'</i> | 8.48 | 8.78 | 8.58 | 8.76 | -0.02 | +0.18 | 8.58 | -0.20 | 0.00 |
| <i>ee'</i> | 8.26 ^b | 8.36 | 8.56 | 8.31 | -0.05 | -0.25 | 8.51 | +0.15 | -0.05 |
| <i>ff'</i> | 8.26 ^b | 8.36 | 8.56 | 8.31 | -0.05 | -0.25 | 8.51 | +0.15 | -0.05 |
| <i>g</i> | 8.26 ^b | 8.22 | | | | | | | |
| <i>h</i> | 8.26 ^b | | 8.22 | | | | | | |
| <i>ii'</i> | 8.26 ^b | | 8.56 | 8.57 | | | 8.51 | | |
| $\Sigma \Delta $ (p.p.m.) | | | | | 0.18 | 0.82 | | 0.78 | 0.18 |

^a Internal standard tetramethylsilane. ^b Centre of eight-proton peak.

TABLE 2
220 MHz Spectra ^a of the tertiary alcohols in pyridine (τ values ^b)

| Protons | 2-Methyl adamantan-2-ol | Predicted <i>cis</i> | Predicted <i>trans</i> | (IIa) | Δ <i>cis</i> (p.p.m.) | Δ <i>trans</i> (p.p.m.) | (IIb) | Δ <i>cis</i> (p.p.m.) | Δ <i>trans</i> (p.p.m.) |
|---------------------------|----------------------------|----------------------|------------------------|-------|---------------------------------|-----------------------------------|-------|---------------------------------|-----------------------------------|
| <i>a</i> ^c | 8.48 | | | 8.47 | | | 8.47 | | |
| <i>bb'</i> | 8.11 | 8.07 | 8.07 | 8.08 | | | 8.08 | | |
| <i>cc'</i> | 7.22 | 7.52 | 7.32 | 7.48 | -0.04 | +0.16 | 7.24 | -0.28 | -0.08 |
| <i>dd'</i> | 8.40 | 8.70 | 8.50 | 8.72 | +0.02 | +0.22 | 8.51 | -0.19 | +0.01 |
| <i>ee'</i> | 8.06 ^d | 8.16 | 8.36 | 8.11 | -0.05 | -0.25 | 8.26 | +0.10 | -0.10 |
| <i>ff'</i> | 8.25 | 8.35 | 8.55 | 8.38 | +0.03 | -0.17 | 8.55 | +0.20 | 0.00 |
| <i>g</i> | 8.20 ^e | 8.16 | | | -0.02 | | | -0.13 | |
| <i>h</i> | 8.10 ^e | | 8.06 | | | +0.08 | | | -0.03 |
| <i>ii'</i> | 8.28 | 8.58 | 8.58 | 8.56 | | | 8.51 | | |
| $\Sigma \Delta $ (p.p.m.) | | | | | 0.16 | 0.88 | | 0.90 | 0.22 |

^a Full assignments were not possible from the 100 MHz spectra. ^b Internal standard tetramethylsilane. ^c Methyl resonance. ^d Deshielded relative to *ff'* by a 1,3-diaxial interaction with the 2-methyl group (E. L. Eliel, M. H. Gianni, T. H. Williams, and J. B. Stothers, *Tetrahedron Letters*, 1962, 741; H. Booth, *Progr. N.M.R. Spectroscopy*, 1969, 5, 242). ^e Both at τ 8.18 in CCl₄; we have assumed that *h* will be more deshielded in pyridine; the extent of deshielding in pyridine (relative to CCl₄) varied from 0.5 p.p.m. for *cc'* to *ca.* 0 for *ii'*.

TABLE 3
Correlation coefficients (ρ)

| Compound | Points | log gradient <i>vs.</i> log <i>R</i> ^a | Slope | Gradient <i>vs.</i> 100/ <i>R</i> ² | Gradient <i>vs.</i> 100/ <i>R</i> ³ | log DEu ^b <i>vs.</i> log <i>R</i> ^a | Slope | DEu ^b <i>vs.</i> 100/ <i>R</i> ² | DEu ^b <i>vs.</i> 100/ <i>R</i> ³ |
|---|--------|--|-------|---|---|--|-------|---|---|
| Adamantan-2-ol ^c | 8 | 0.992 | 1.85 | 0.990 | 0.985 | 0.991 | 1.95 | 0.993 | 0.990 |
| Adamantan-2-ol ^d | 8 | 0.993 | 1.91 | 0.998 | 0.997 | 0.990 | 2.00 | 0.996 | 0.997 |
| { (Ia) <i>cis</i> | 8 | 0.992 | 1.94 | 0.998 | 0.997 | 0.992 | 1.97 | 0.997 | 0.996 |
| { (Ia) <i>trans</i> | 8 | 0.929 | 1.74 | 0.981 | 0.988 | 0.924 | 1.75 | 0.979 | 0.986 |
| { (Ia) known protons | 6 | 0.991 | 1.91 | 0.997 | 0.998 | 0.990 | 1.94 | 0.997 | 0.996 |
| { (Ib) <i>cis</i> | 8 | 0.904 | 1.89 | 0.975 | 0.977 | 0.894 | 1.89 | 0.971 | 0.974 |
| { (Ib) <i>trans</i> | 8 | 0.995 | 1.99 | 0.998 | 0.995 | 0.991 | 2.00 | 0.996 | 0.993 |
| { (Ib) known protons | 6 | 0.994 | 1.93 | 0.998 | 0.998 | 0.988 | 1.93 | 0.996 | 0.996 |
| $\Sigma(\rho - \rho$ known protons) ^e | | 2(-152) | | 1(-39) | -4(-31) | 5(-160) | | 0(-43) | -3(-32) |
| 2-Methyl- adamantan-2-ol ^f | 9 | 0.986 | 1.91 | 0.994 | 0.994 | | | | |
| { (IIa) <i>cis</i> | 9 | 0.959 | 2.09 | 0.982 | 0.977 | 0.956 | 2.09 | 0.983 | 0.978 |
| { (IIa) <i>trans</i> | 9 | 0.972 | 2.04 | 0.981 | 0.977 | 0.976 | 2.05 | 0.983 | 0.979 |
| { (IIa) known protons | 7 | 0.989 | 1.91 | 0.985 | 0.980 | 0.988 | 1.93 | 0.986 | 0.981 |
| { (IIb) <i>cis</i> | 9 | 0.955 | 1.93 | 0.988 | 0.988 | 0.957 | 1.93 | 0.988 | 0.988 |
| { (IIb) <i>trans</i> | 9 | 0.991 | 1.93 | 0.995 | 0.994 | 0.990 | 1.93 | 0.995 | 0.994 |
| { (IIb) known protons | 7 | 0.992 | 1.92 | 0.996 | 0.995 | 0.992 | 1.93 | 0.996 | 0.995 |
| $\Sigma(\rho - \rho$ known protons) ^e | | -31(-54) | | -4(-12) | -4(-10) | -34(-43) | | -4(-11) | -4(-9) |

^a Proton-oxygen distance. ^b As defined by Paasivirta,^{8a,w} DEu (secondary alcohols) is the average value of 100 [induced shift of proton/induced shift of α -proton (*a*)]; DEu (tertiary alcohols) is the average value of 100 (induced shift of proton/induced shift of *cc'*) (DEu value for *cc'* in the corresponding secondary alcohol). ^c Gradient shift data and *R* values of Cockerill and Rackham; ^{8a} DEu values from work by Wahl and Peterson.^{8c} ^d As footnote (c) but our *R* values. ^e For the new assignments (connected by outer braces); figures in parentheses are those for old assignments (connected by inner braces). ^f Data of Fleming and Hanson.⁹

here, that (Ia) and (IIa), and (Ib) and (IIb), had a common relationship between the hydroxy and 5-methyl groups.] We have been able to do this in three ways, all making use of tris(dipivaloylmetanato)europium-(III)⁷ in [²H]chloroform. Data obtained by use of this shift reagent can be handled in various ways,^{7a,8} and we have employed several here. A log gradient (of chemical shift *vs.* concentration of complex) *vs.* log (proton-oxygen distance) plot is illustrated (Figure 1), and other methods are listed in Table 3; all gave essentially the same result. The assignments of adamantan-2-ol first suggested by van Deursen and Korver² have been used by others to elucidate the europium-expanded spectra of adamantan-2-ol⁸ⁱ and 2-methyladamantan-2-ol;⁹ we checked these assignments by extrapolation to zero concentration of the plots of chemical shift *vs.* concentration of complex; these clearly showed the downfield and upfield methylene protons to be *cc'* and *dd'* (and not *ee'* and *ff'*, which would reverse our present assignments of *cis* and *trans*). The best results were obtained from use of proton-oxygen distances (*R*), and not estimated distances to the europium atom, and indicated a relationship between induced shift and $1/R^2$, as observed by other workers in systems with spatially fixed protons.^{8b, l, r, w} Interatomic distances were measured from Dreiding models, which should be unusually accurate in these molecules.* Precision of fit is best judged by the correlation coefficients obtained for the two model compounds, and for those protons whose assignment is not in doubt

* Our measurements (Table 4) differ from those published,^{8j} mainly in reversing the distances for protons *ee'* and *ff'* (4.9 *cis* and 4.9 *trans*). A log gradient-log *R* plot for adamantan-2-ol from the shift data of Cockerill and Rackham⁸ⁱ and our *R* values has a correlation coefficient of 0.993 and a gradient of -1.9. The *R* values of Goodisman and Matthews^{8j} when used with these shift data give a correlation coefficient of 0.971 and a gradient of -1.85. We believe the shift data of Cockerill and Rackham⁸ⁱ for adamantan-2-ol to be more useful than those of Wahl and Peterson,^{8e} as the latter are based on measurements at only one concentration of europium complex. Consequently we repeated the work of Goodisman and Matthews;^{8j} since the distance $R'(H-Eu)$ will in general be greater than *R*, one can write $R' = R + d$ and this work involved finding the value of *d* for which a plot of log gradient *vs.* log (*R* + *d*) had a slope of -3. For *d* = 2.1 Å the slope was -3 and the correlation coefficient 0.990. The shift data of Wahl and Peterson^{8e} require a value for *d* of 3.5 Å, to give a slope of -3 with a correlation coefficient of 0.984. If we use the value for *d* of 2.1 Å, and an oxygen-europium distance equal to the sum of the covalent radii (2.6 Å), the O-Eu-H angle is found to lie between 25 and 30° for all the protons considered in the four isomers.

⁷ (a) C. C. Hinkley, *J. Amer. Chem. Soc.*, 1969, **91**, 5160; (b) J. K. M. Sanders and D. H. Williams, *Chem. Comm.*, 1970, 422.

⁸ (a) E. R. Birnbaum and T. Moeller, *J. Amer. Chem. Soc.*, 1969, **91**, 7274; (b) P. V. Demarco, T. K. Elzey, R. B. Lewis, and E. Wenkert, *ibid.*, 1970, **92**, 5735, 5737; (c) J. K. M. Sanders and D. H. Williams, *ibid.*, 1971, **93**, 641; (d) C. C. Hinkley, M. R. Klotz, and F. Patil, *ibid.*, 1971, **93**, 2417; (e) G. H. Wahl and M. R. Peterson, *Chem. Comm.*, 1970, 1167; (f) J. Briggs, F. A. Hart, and G. P. Moss, *ibid.*, 1970, 1506; (g) P. Bélanger, C. Freppel, D. Tizané, and J. C. Richer, *ibid.*, 1971, 266; (h) J. Briggs, F. A. Hart, G. P. Moss, and E. W. Randall, *ibid.*, 1971, 364; (i) S. Farid, A. Ateya, and M. Maggio, *ibid.*, 1971, 1285; (j) J. Goodisman and R. S. Matthews, *ibid.*, 1972, 127; (k) J. W. ApSimon and H. Beierbeck, *ibid.*, 1972, 172; (l) A. F. Cockerill and D. M. Rackham, *Tetrahedron Letters*, 1970, 5149; 5153; (m) L. H. Keith, *ibid.*, 1971, 3; (n) C. Beauté,

in the four alcohols under discussion. The worst correlation coefficient among six ways of treating each of these six sets of data is 0.980, and that involves

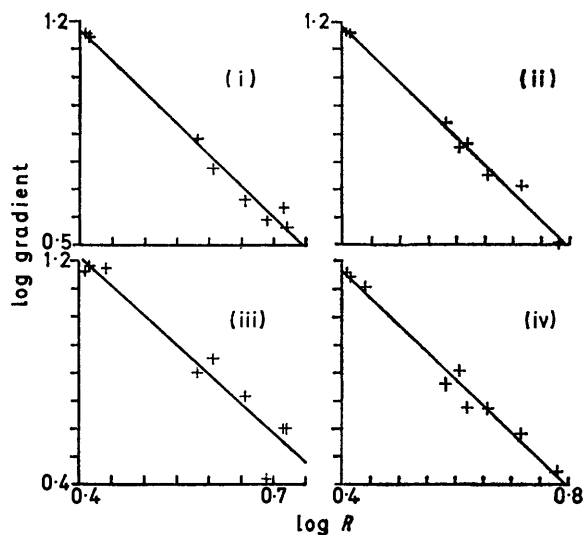


FIGURE 1a Plot of log gradient (of shift *versus* europium concentration) *versus* log *R*. Revised assignments: (i), (Ia) as *cis*; (ii), (Ib) as *trans*; (iii), (IIa) as *cis*; (iv), (IIb) as *trans*

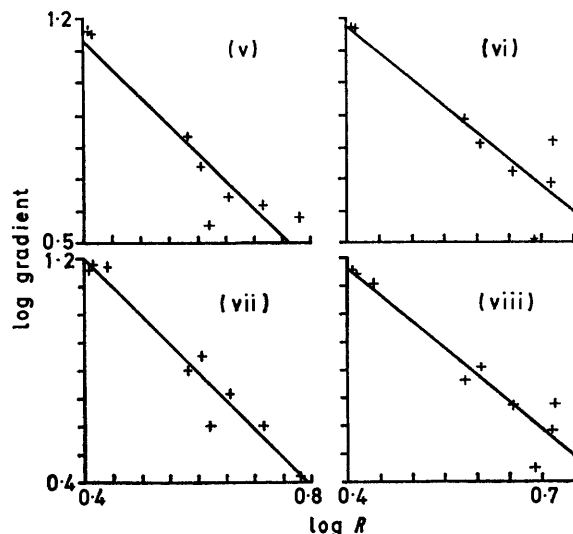


FIGURE 1b Plot of log gradient (of shift *versus* europium concentration) *versus* log *R*. Reversed assignments, previously published for (v), (Ia) as *trans*; (vi), (Ib) as *cis*; (vii), (IIa) as *trans*; (viii), (IIb) as *cis*

the inverse-cube H-O relationship which is negated by the log-log plot; there is little in the figures to justify use of this inverse-cube relationship; the log-log

Z. W. Wolkowski, and N. Thoai, *ibid.*, 1971, 817; (o) Z. W. Wolkowski, *ibid.*, 1971, 825; (p) W. Walter, R. F. Becker, and J. Thieni, *ibid.*, 1971, 1971; (q) P. Kristiansen and T. Ledaal, *ibid.*, 1971, 2817, 4457; (r) A. J. Rafalksi, J. Barciszewski, and M. Wiewiórowski, *ibid.*, 1971, 2829; (s) R. Caple and S. C. Kuo, *ibid.*, 1971, 4413; (t) I. Armitage, G. Dunsmore, L. D. Hall, and A. G. Marshall, *Chem. and Ind.*, 1972, 79; (u) H. Huber and C. Pascual, *Helv. Chim. Acta*, 1971, **54**, 913; (v) J. Paasivirta, *Suomen Kem.*, 1971, **B44**, 131, 135; (w) J. Paasivirta and P. J. Mälkönen, *ibid.*, 1971, **B44**, 230, 283.

* I. Fleming and S. W. Hanson, personal communication.

plots have a gradient within experimental error of -2 , as is assumed in the gradient *vs.* $100/R^2$ relationship.

When the correlation-coefficient method is used to assign configurations, the best parameter appears to be the difference between correlation coefficients obtained for all protons of each isomer, and that which results from inclusion of only the six or seven protons per isomer of undisputed assignment. All six treatments lead to the same conclusions, but with very different degrees of force in the secondary and tertiary pairs. In the secondary pair the assignment already favoured on the grounds of additivity increments ($a = cis$, $b = trans$) is decisively preferable to the contrary

to be considered, and cannot be because the position of the europium atom is unknown, and (evidently) variable.

We finally employed decoupling experiments on the expanded spectra. The signal from the bridgehead proton at g or h approximates to a regular heptet (Figure 2), long-range coupling being small and insignificant. The six protons (in three pairs) vicinally coupled to this proton are therefore ii' , ee' , and ff' for the *cis*-isomers and ii' , cc' , and dd' for the *trans*-isomers. For the tertiary isomer a , irradiation at the frequency of cc' caused collapse of the dd' signal only, and irradiation at the frequency of ee' caused collapse of

TABLE 4

Normalised ^a least-square gradient values ^b

| Protons | $R/\text{\AA}^c$ | Adamantan-2-ol ^d | (Ia) | (Ib) | 2-Methyl adamantan-2-ol ^e | (IIa) | (IIb) |
|---------|------------------|-----------------------------|--------------|------------|---|--------------|--------------|
| a | (2.76) f | 100 | 100 | 100 | (54) | (60.5) | (52.5) |
| bb' | 2.60 | 59 | 58 | 58.5 | 59 | 62 | 57 |
| cc' | 2.56 | 60.5 | 59 | 59 | 60.5 | 59 | 59 |
| dd' | 3.82 | 28.5 | 27.5 | 27.5 | 24.5 | 26 | 24 |
| ee' | 4.04 | 22.5 | 22.5 | 23 | 27.5 | 29 | 26.5 |
| ff' | 4.53 | 19 | 18 | 18 | 20 | 21.5 | 19.5 |
| g | 4.17(4.89) f | 15 | } 14.5(15.5) | } 23.5(10) | } 17 | } 16.5(10.5) | } 19.5(11.5) |
| h | 5.25(6.03) f | 24 | | | | | |
| ii' | 5.19 | 17 | 17 | 16.5 | 16 | 16.5 | 15.5 |

Figures in parentheses are for methyl groups.

^a Ref. 8*w*. ^b Standard errors $\leq 4\%$; our gradient data are based on 4—5 points over a range of [europium]/[alcohol] of 0.25—0.85; no plot showed curvature. ^c $\pm 0.05 \text{\AA}$. ^d Data of ref. 8*l*. ^e Data of ref. 9. f Measuring to the centre of the circle described by the three protons.

assignment previously published,⁴ giving correlation coefficients (whole molecule) quite as good as those observed for known protons in the same molecules, or for adamantan-2-ol itself, whereas the alternative hypotheses are worse by any treatment. Moreover, the gradients observed for the lone bridgehead protons (g or h) in the a and b isomers have values (Table 4) very close to those of the two protons assigned as g and h , respectively, in adamantan-2-ol by Wahl and Peterson^{8*e*} and Cockerill and Rackham,^{8*l*} while the data for the methyl protons move in the opposite sense, as expected.

In the tertiary series, however, the evidence is not as easily rationalised, although assignment follows naturally from the convincing secondary assignments (the impossible conclusion that *both* isomers are *trans* would give least disagreement with predictions!). If anything $a = cis$, $b = trans$, as now preferred on other grounds, is preferable to the alternative; the reason for the dilemma is that *both* the methyl group *and* the proton determining the stereochemistry (g and h), have a larger relative shift in one isomer (b) than they have in the other (a). Our simplified approach is incapable of dealing with this anomaly; obviously the angle effect in the pseudo-contact-shift expression¹⁰ needs

both the ff' and the bridgehead proton signals; similarly for isomer b collapse of the bridgehead proton signal was achieved by irradiation at the frequency of cc' and not of ee' (Figure 2). For isomer b double irradiation at the frequencies of ii' and cc' gave a better decoupling of the bridgehead proton, but this could not be used in isomer a owing to the proximity of the ii' signal to that of the bridgehead proton. This constituted conclusive proof of the preferred assignments ($a = cis$, $b = trans$) in the tertiary isomers; similar decoupling experiments on the secondary isomers were not as conclusive owing to proximity and accidental overlap of resonances. Here, however, no need existed for confirmation of already clear conclusions.

To summarise; the isomers denoted a are *cis*, and those denoted b are *trans*; these conclusions are established independently of the work of van Deursen and Korver,² which they now indirectly confirm; the evidence used in tentative assignments by Bone and Whiting⁴ must be otherwise interpreted.

It is now possible to go back and to evaluate the alternative methods used in reaching these conclusions. The additivity principle¹ [method (i)] in estimating chemical shifts is confirmed as simple to use and accurate in all cases, however it does rely extensively on literature assignments.² The use of a correlation coefficient for distances from various protons to oxygen,

¹⁰ H. M. McConnell and R. F. Robertson, *J. Chem. Phys.*, 1958, **29**, 1361.

estimated from measurements of Dreiding models and the ratios of chemical shifts to europium concentration [method (ii)] is remarkable for the high correlation coefficients obtained for wrong as well as for right hypothetical constitutions. It is certainly unsafe to use this method in such cases unless both isomers are available and both of the two contradictory hypotheses are

correlations with those for protons previously assigned in the model compounds [method (iii)] produced the same conclusions as method (ii). The defeat of methods (ii) and (iii) in the tertiary cases proved to be due to the misbehaviour of one line in the spectrum, that due to the 5-methyl group, which did not behave as though its three protons were concentrated at their mid-point;

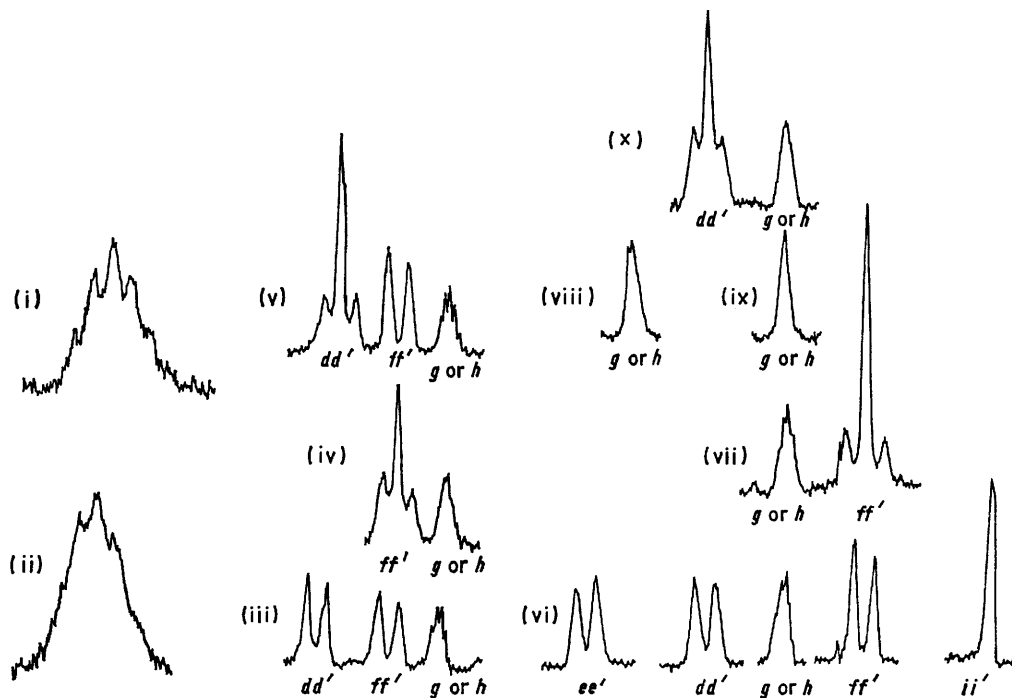


FIGURE 2 (i), Expansion of lone bridgehead proton (*g* or *h*) in (IIa); (ii), expansion of lone bridgehead proton (*g* or *h*) in (IIb); (iii), europium expanded spectrum of (IIa); (iv), irradiation of *ee'* in expanded spectrum of (IIa); (v), irradiation of *cc'* in expanded spectrum of (IIa); (vi), europium expanded spectrum of (IIb); (vii), irradiation of *ee'* in expanded spectrum of (IIb); (viii), irradiation of *ii'* in expanded spectrum of (IIb); (ix), irradiation of *ii'* and *cc'* in expanded spectrum of (IIb); (x), irradiation of *cc'* in expanded spectrum of (IIb)

treated fairly and objectively; in agreement with prevailing opinion^{8*l,v,w*} we find the relationship of gradient (of shift *vs.* europium concentration) or relative shift^{8*v,w*} (DEu) *versus* $100/R^2$ to be slightly the best of the six comparably justifiable treatments. These methods gave excellent results for the secondary isomers but a very weak preference for the tertiary compounds (and are independent of previous work). The comparison of the gradients obtained from the least-squares

possibly this assumption ought to be avoided in future. Finally, spin-decoupling of the europium-shifted spectra at 100 MHz [method (iv)] provided conclusive evidence in the tertiary series and presented no difficulty of execution or interpretation; in the secondary series its evidence was inconclusive, but compatible with the clear conclusion from methods (i)–(iii).

[2/904 Received, 24th April, 1972]