J. Chem. Soc. (B), 1970

Studies in Nuclear Magnetic Resonance Spectroscopy. Part VIII.¹ Conformations and Coupling Constants in 1,2-Disubstituted 3,3-Dimethylbutanes

By L. M. Jackman*† and D. P. Kelly, Organic Chemistry Department, The University of Melbourne, Victoria. Australia

The 100 MHz spectra of a series of 1,2-disubstituted 3,3-dimethylbutanes have been analyzed exactly as ABC systems by use of iterative computer techniques. The chemical shifts are shown to agree reasonably well with those predicted from systems with similarly oriented substituents. The gauche (J_g) and trans (J_i) coupling constants were shown to be of the same sign and opposite in sign to J_{gem}. The values of the vicinal coupling constants and their relative insensitivity to concentration change suggest that these compounds exist predominantly as single conformers, viz. with gauche oriented 1,2-substituents. Neither J_a nor J_t correlates with the electronegativities or sizes of the substituents. Small differences observed in these parameters in this series of compounds may therefore reflect different relative populations of conformers.

WE have observed ¹ that 2,2-dimethylpentan-3-ol exists predominantly, if not exclusively, as a single conformer [Figure 1 (II); (X = Me, Y = OH)]. This conclusion



FIGURE 1 Conformations of 1,2-disubstituted-3,3-dimethylbutanes

was based on the fact that the n.m.r. parameters changed only slightly over the concentration range 1-100% and that the values of the vicinal coupling constants corresponded to the trans $(J_t \ 10 \ \text{Hz})$ and gauche $(J_q$ 2 Hz) interactions. This, together with reports that J_{q} in some halogenoalkanes may be negative in sign,^{2,3} prompted us to analyse the ABC type spectra of a number of 1,2-disubstituted 3,3-dimethylbutanes. Although J_{a} was found to be small and positive in the case of the alcohol, it was considered possible that increasing the electronegativity of the substituents X

and Y might reduce J_g to a negative value.⁴ Accordingly, the spectra of the corresponding 1,2-dichloro-, 1,2-dibromo-, 2-chloro-1-iodo-, 2-bromo-1-iodo-, and 1-bromo-2-hydroxy-derivatives were investigated.

The possibility that J_q may be negative was tested in each case by assigning the spectrum firstly with J_{gem} only negative and secondly with both J_{gem} and J_g negative. The iterated parameters and computed spectra for the dibromide appear in Figure 2.[‡] Comparison of the intensities shows that J_g is not negative. Similarly, the gauche vicinal coupling constants for the other compounds in the series were found to be positive. The parameters which best reproduce the observed spectra are assembled in Table 1. However, these findings do not prove that J_g can never be negative, since J_{vic} depends not only upon the electronegativity of the substituent, but also upon its orientation.⁵ If the compound were in conformation (I), J_g would be expected to be a minimum as there would be an antiperiplanar relationship between the bond to the substituent and part of the 'coupling path' between the two protons. This may explain the observed lack of sensitivity of coupling constants in 1,2-dihalogenoethanes to the electronegativity of the substituents.⁶

³ H. S. Gutowsky, G. G. Belford, and P. E. McMahon, J. Chem. Phys., 1962, **36**, 3353.

⁴ J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolu-tion Nuclear Magnetic Resonance Spectroscopy,' Pergamon, London, 1966, vol. 2, p. 680.

H. Booth, Tetrahedron Letters, 1965, 411.

⁶ R. J. Abraham, L. Cavalli, and K. G. R. Pachler, Mol. Phys., 1966, 11, 471.

[†] Present address: Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802. [‡] The lines drawn at the top of the Figures only indicate the

correct transitions, their spacings are not the spectral parameters.

¹ Part VII, L. M. Jackman and D. P. Kelly, preceding paper. ² H. Finegold, J. Chem. Phys., 1964, 41, 1808.

TABLE 1 Iterated n.m.r. parameters for 1,2-disubstituted 3,3-dimethylbutanes^a

				r		,	5		
Bu ^t CHR ¹ -CH ₂ R ²									
R1	\mathbf{R}^{2}	Concn.	δ(Α)	δ (B)	δ(C)	$\delta(\operatorname{But}) d$	J_{AB} (Hz)	J_{AC} (Hz)	J_{BC} (Hz)
OH	Me	100 b	$302 \cdot 83 \pm 0 \cdot 01$	$154{\cdot}09\pm0{\cdot}02$	$124{\cdot}28\pm0{\cdot}02$	88.4	1.96 ± 0.02	10.61 ± 0.03	-13.81 ± 0.02
		10	$299{\cdot}64 \pm 0{\cdot}01$	$152{\cdot}56\pm0{\cdot}02$	$119{\cdot}45\pm0{\cdot}02$	87.0	1.98 ± 0.02	10.30 ± 0.03	-13.45 ± 0.02
\mathbf{Br}	Br	100 °	$404 \cdot 19 + 0 \cdot 11$	396.67 + 0.11	$354 \cdot 74 \pm 0 \cdot 10$	$111 \cdot 4 \pm 0 \cdot 5$	2.85 ± 0.17	9.58 ± 0.17	-11.49 ± 0.17
		20 f				_	3.08	9.26	-11.37
		10	$399{\cdot}54\pm0{\cdot}05$	$390{\cdot}53\pm0{\cdot}05$	$352 \cdot 96 \pm 0 \cdot 05$	113.5 ± 1.0	3.08 ± 0.08	$9{\cdot}10\pm0{\cdot}08$	$-11\cdot40\pm0\cdot08$
		1	$398{\cdot}31\pm0{\cdot}03$	$388\cdot75\pm0\cdot03$	$352{\cdot}54\pm0{\cdot}03$	114.5 ± 1.0	3.62 ± 0.05	$9{\cdot}13\pm0{\cdot}04$	-11.39 ± 0.04
C1	Cl	100 0	$382 \cdot 70 + 0 \cdot 06$	$394 \cdot 28 + 0 \cdot 06$	$354 \cdot 11 + 0 \cdot 05$	105.8 ± 1.0	2.56 ± 0.1	9.36 ± 0.09	-11.52 ± 0.08
		10	$378 \cdot 27 \stackrel{\frown}{\pm} 0 \cdot 04$	$387 \cdot 98 \stackrel{-}{\pm} 0 \cdot 04$	$352{\cdot}42 \stackrel{+}{\pm} 0{\cdot}04$	$108\cdot 2 \stackrel{-}{\pm} 1\cdot 0$	3.05 ± 0.08	9.23 ± 0.07	-11.93 ± 0.07
		1	$377{\cdot}50 \pm 0{\cdot}01$	$386 \cdot 66 \pm 0 \cdot 1$	$352{\cdot}18\pm0{\cdot}01$	109.3 ± 1.0	3.07 ± 0.02	9.03 ± 0.02	-11.83 ± 0.02
Cl	I	100 ¢	$415 \cdot 11 + 0 \cdot 10$	393.38 ± 0.10	376.76 + 0.10	115.4 + 1.0	3.44 + 0.14	8.92 ± 0.14	-12.31 + 0.15
		50	$413 \cdot 37 + 0.03$	$391 \cdot 37 \pm 0.03$	$376\cdot39 \pm 0.03$	h	3.78 ± 0.04	8.77 ± 0.04	$-12\cdot24 \pm 0\cdot04$
		10	412.01 ± 0.11	390.04 ± 0.10	377.79 ± 0.10	$118 \cdot 4 \pm 1 \cdot 0$	4.11 ± 0.14	8.37 ± 0.13	$-12 \cdot 27 \pm 0 \cdot 15$
		1	$410{\cdot}72\pm0{\cdot}08$	$388\cdot78\pm0\cdot07$	$377 \cdot 21 \pm 0 \cdot 07$	h	4.09 ± 0.10	8.40 ± 0.10	$-12 \cdot 27 \pm 0 \cdot 11$
Br	I	3·3 ø	417.91 ± 0.03	$390{\cdot}44 \pm 0{\cdot}03$	$365{\cdot}27 \pm 0{\cdot}03$	116.9 ± 0.2	3.89 ± 0.04	8.75 ± 0.04	$-11{\cdot}46\pm0{\cdot}04$
OH	Br	100 g	401.96 + 0.04	$396 \cdot 86 + 0 \cdot 04$	$374 \cdot 45 + 0 \cdot 04$	107.6 + 0.2	3.14 ± 0.05	8.90 ± 0.05	$-12{\cdot}49\pm0{\cdot}05$
		10	$\textbf{399.07} \pm \textbf{0.02}$	$382 \cdot 64 \pm 0.02$	$369{\cdot}61 \pm 0{\cdot}02$	110.4 ± 0.2	3.05 ± 0.02	8.68 ± 0.02	-12.45 ± 0.03
		1	$399{\cdot}29 \stackrel{-}{\pm} 0{\cdot}04$	$379{\cdot}64 \ \pm 0{\cdot}03$	$368 \cdot 27 \pm 0 \cdot 03$	$110\cdot2\pm0\cdot2$	2.83 ± 0.05	8.78 ± 0.05	$-12{\cdot}45\pm0{\cdot}05$
Chaminal chifte in II. downfall form internal Ma Ci at 100 MIT-						h Concentrations on 0/ why in CCl & Other perameters			

^a Chemical shifts in Hz downfield from internal Me₄Si at 100 MHz. ^b Concentrations, ca. % w/v in CCl₄. ^c Other parameters are: $100\% \ \delta(\mathbb{R}^2) \begin{cases} 100 \cdot 26 \pm 0 \cdot 02 \\ 96 \cdot 40 \pm 0 \cdot 02 \end{cases} \int_{A\mathbb{R}^2} \begin{cases} -0 \cdot 23 \pm 0 \cdot 02 \\ -0 \cdot 11 \pm 0 \cdot 01 \end{cases} \int_{B\mathbb{R}^2} \begin{cases} 7 \cdot 47 \pm 0 \cdot 01 \\ 7 \cdot 45 \pm 0 \cdot 01 \end{cases} \int_{C\mathbb{R}^2} \begin{cases} 7 \cdot 35 \pm 0 \cdot 02 \\ 7 \cdot 39 \pm 0 \cdot 02 \end{cases}$ The spectrum of a 1% solution is identical (except for OH signal) to that of a 10% solution so the parameters are unchanged. ^d Not iterated. ^e Concentrations, ca. % w/w in CCl₄. ^f From 60 MHz data; ref. 8. ^g Concentrations ca. % v/v in CCl₄. ^h Not measured. ⁱ % v/v in CCl₄-ether (80 : 6).

ដំរ 317 (a) (b)

FIGURE 2 Observed and computed ABC proton region of 100 MHz spectrum of 1,2-dibromo-3,3-dimethylbutane (neat)

Computed parameters are (a) ν_{A} , 404·195; ν_{B} , 396·675; ν_{C} , 354·743; J_{AB} , 2·851; J_{AC} , 9·576; J_{BC} , -11·488 Hz. (b) ν_{A} , 405·119; ν_{B} 396·030; ν_{C} , 354·458; J_{AB} -2·941; J_{AC} , 8·406; J_{BC} -10·065 Hz.

The values of J_q and J_t in Table 1 indicate that all compounds are predominantly in one conformation, viz. (II). During this work the same conclusion was reached,

7 M. Buza and E. I. Snyder, J. Amer. Chem. Soc., 1966, 88, 1161.

 ⁸ E. I. Snyder, *J. Amer. Chem. Soc.*, 1966, 88, 1155.
 ⁹ C. A. Kingsbury and D. C. Best, *J. Org. Chem.*, 1967, 32, 6.
 ¹⁰ N. L. Allinger, J. A. Hirsch, M. A. Miller, I. J. Tyminski, and F. A. Van-Catledge, J. Amer. Chem. Soc., 1968, 90, 1199.

in the case of the dibromo-compound, by Buza and Snyder,⁷ who analysed the 60 MHz spectrum of the 1,2dibromo-1-deuterio-derivative. They found J(HH)10 Hz, which can only correspond to a trans-orientation of protons [*i.e.* (II; $H_B = D$, X = Y = Br)]. Snyder also showed that the coupling constants alter very little in solvents of widely varying dielectric constant.⁸ The small changes that are observed in carbon tetrachloride and acetone (CCl₄: J_g 3.08, J_t 9.26; Me₂CO: J_g 2.64, J_t 9.91) do however suggest that the dibromide populates conformation (II) in acetone solution even more heavily than in carbon tetrachloride since, owing to their higher polarity, gauche conformations are more favoured in more polar solvents.² gauche Orientations of bulky substituents are apparently more stable than originally believed, as demonstrated by the conformations of threo- and erythro-3,4-dibromo-2,2-dimethylpentane 9 (bromines gauche to each other) and the calculations of Allinger and his co-workers.¹⁰

In order to determine the extent to which the vicinal coupling constants reflect conformations, it is necessary to know the influence on the vicinal coupling constant of both the electronegativity and the size of the substituent [increasing the bulk of R1 and R2 should decrease the value of J_g (dihedral angle $\rightarrow 90^{\circ}$)]. The effect of electronegativity on J_{vic} has been studied by a number of workers ¹¹ and the relationship $J_{av} = 17.97$ – $0.796\Sigma E$ has been obtained for a large range of compounds.^{12c} As we are concerned in this series of

¹¹ (a) C. N. Banwell and N. Sheppard, Discuss. Faraday Soc., ¹¹ (a) C. N. Banwell and N. Sheppard, Discuss. Fardary Soc., 1962, 34, 115; (b) R. E. Glick and A. A. Bothner-By, J. Chem. Phys., 1956, 25, 362; (c) R. G. Abraham and K. G. R. Pachler, Mol. Phys., 1963, 7, 165; (d) S. L. Stafford and J. D. Baldeschwieler, J. Amer. Chem. Soc., 1961, 83, 4473.
¹² (a) J. R. Cavanaugh and B. P. Dailey, J. Chem. Phys., 1961, 34, 1099; (b) G. V. D. Tiers, 'Characteristic N.M.R. Shielding Values for Hydrogen in Organic Structures,' Minnesota Mining and Manufacturing Company. Saint Paul 1958

and Manufacturing Company, Saint Paul, 1958.



compounds with a range of electronegativities of unity $(\Sigma E 5.5-6.5)$, it is not surprising that no correlation exists between J_t or J_g and ΣE . Huitric and his-coworkers 13 found that in systems of fixed geometry (1-substituted cis- and trans-2-aryl [3,3,6,6-2H₄]cyclohexane) the substituent effect for both $J_t(ax,ax)$ and J_g





(ax,eq) is opposite to the normally accepted decrease in J with increasing electronegativity of the substituent. Also, in both cases (cis and trans) the increase in Jwith substituents of different electronegativity (e.g. OH and NO₂) is approximately the same, despite the fact that in the cis-compound alone an antiperiplanar relationship exists between the substituent and the proton-proton coupling path. A similar increase in J_q $(J_{1,2})$ with substituent electronegativity was found in 1,2-disubstituted 4-t-butylcyclohexanes,14 although in these compounds the 1- and 2-substituents were the same. There also appears to be no correlation with the size of the substituents and J_{vic} in this limited series of compounds. The small variations observed in the coupling constants may therefore reflect differences in the relative populations of conformers, such that the population of conformer (II) decreases in the order (Y, X) OH, Me > Cl, Cl > Br, Br; OH, Br > Br, I; Cl, I.

2-Chloro-1-iodo- and 2-bromo-1-iodo-3,3-dimethylbutane were prepared from t-butylethylene by the addition of iodine monochloride and iodine monobromide, respectively. It is assumed that the addition occurs with the normal Markownikoff orientation. However, additional support is available from a consideration of chemical shifts in this series of compounds.

The spectra of the dichloro-compound are significantly different from those of the corresponding dibromide in that the chemical shift differences between the three protons are smaller and that the methine proton is no longer at lowest field (Figure 3). This upfield shift of 0.2 p.p.m. for the methine proton may be empirically predicted from a consideration of the chemical shifts of isopropyl¹² and adamantyl compounds¹⁵ (Table 2). The former provide an increment for the



effect of geminal substituents on the methine proton whereas the latter provide one for the effect of gaucheorientated vicinal substituents on methylene protons.



FIGURE 4 Observed and computed ABC proton region of 100 MHz spectrum of 2-chloro-1-iodo-3,3-dimethylbutane (neat)

The chemical shift differences may be computed from the parent alkane (where a comparison between a methine proton and a methylene proton would be required), but a more accurate prediction is obtained by referencing the predicted shifts to the dibromide. Thus the predicted shift for the dichloride is 3.99 - [(4.21 -(4.14) + (2.30 - 2.11) = 3.73 p.p.m. For the 2-chloro-

A. C. Huitric, J. B. Carr, W. F. Trager, and B. J. Nist, Tetrahedron, 1963, 19, 2145.
 ¹⁴ S. Wolfe and J. R. Campbell, Chem. Comm., 1967, 872.

¹⁵ R. C. Fort and P. R. Schleyer, J. Org. Chem., 1965, 30, 789.

¹⁶ K. W. Bartz and N. F. Chamberlain, Analyt. Chem., 1964, 36, 2151.

1-iodo-compound the estimated shift is 0.26 p.p.m. downfield from that of the dibromide, whereas for the 1-chloro-2-iodo compound the signal is 0.16 p.p.m. upfield. The observed downfield shift confirms that the spectrum in Figure 4 is that of the normal Markownikoff addition product. A similar argument can be advanced for the iodo-bromo-compound (Figure 5) although it is less conclusive in this case.



FIGURE 5 Observed and computed ABC proton region of 100 MHz spectrum of 2-bromo-1-iodo-3,3-dimethylbutane (ca. 3%)



FIGURE 6 Observed and computed ABC proton region of 100 MHz spectrum of 1-bromo-2-hydroxy-3,3-dimethylbutane (neat)

The inconsistency for line 10 in the observed and computed spectra of 1-bromo-2-hydroxy-3,3-dimethylbutane (Figure 6) is probably due to an underlying impurity, since the compound was known to be impure and the relative intensities of the other lines are correct.

EXPERIMENTAL

The spectra were recorded and analysed by computer techniques (LAOCN3) described previously.¹⁷ In all cases the 'average deviation' between the observed and calculated frequencies was less than 0.13 Hz.

1,2-Dibromo-3,3-dimethylbutane.-This was prepared by the addition of bromine to 3,3-dimethylbut-1-ene at -10°

* Prolonged heating causes decomposition, readily observed by formation of an intense brown-red colour.

† The compound appeared to decompose when prolonged (spinning band) fractionation was attempted.

17 D. P. Kelly, J. Mol. Spectroscopy, 1968, 28, 204.

18 W. H. Puterbaugh and M. S. Newman, J. Amer. Chem. Soc., 1957, 79, 3469.

and purified on a spinning band column; b.p. 88-89°/ 18—20 mm., $n_{\rm D}^{22\cdot5}$ 1.5058 (lit.,¹⁸ b.p. 85°/12 mm., $n_{\rm D}^{20}$ 1.5055).

1,2-Dichloro-3,3-dimethylbutane.-This was prepared in a similar manner; b.p. 63.5°/20 mm., n_D^{22.5} 1.4541 (lit.,¹⁹ b.p. $52^{\circ}/11$ mm., $n_{\rm p}^{20}$ 1.4538).

2-Chloro-1-iodo-3,3-dimethylbutane.-Iodine monochloride (40 g.) in carbon tetrachloride (100 ml.) was added during 2 hr., at -20°, to 3,3-dimethylbut-1-ene (20 ml.) in carbon tetrachloride (100 ml.). The red-brown solution was stirred overnight, washed with saturated sodium hydrogen sulphite solution (colour removed) and dried (MgSO₄) (colour redeveloped). The solvent (coloured) was removed in vacuo and the red liquid distilled rapidly at low pressure * to yield a pink liquid, 2-chloro-1-iodo-3,3-dimethylbutane, b.p. 36.5°/0.45 mm., m.p. ca. 2°, n_p^{24.5} 1.5234; n.m.r. spectra, see above; v_{max.} (film) 2925s, 1460m, 1425m, 1390m, 1360s, 1320m, 1265m, 1225s, 1115s, 908s, 730s, and 578s cm.⁻¹, $m/e \ 248(M + 2, 5\%), \ 247 \ (M + 1, \ ca. \ 2\%), \ 246 \ (M, \ 15\%),$ 121 (M - 125, 24%), 119 (M - 127, 73%), 83 (M - 163, 123%)100%), 77 (36%), and 69(72%) (Found: C, 29.6; H, 4.9; Cl, 14.1; I, 51.2. C₆H₁₂ClI requires C, 29.2; H, 4.9; Cl, 14·4; I, 51·5%).

2-Bromo-1-iodo-3,3-dimethylbutane.-Iodine bromide in carbon tetrachloride was added dropwise to 3,3-dimethylbut-1-ene in carbon tetrachloride at 0°. The mixture was stirred overnight at 0°, then subjected directly to n.m.r. analysis, as any attempt to isolate the compound resulted in decomposition. The spectrum showed that ca. 45% of the olefin remained. The concentration of the (assumed) 2-bromo-1-iodo-3,3-dimethylbutane was 3.3% by volume.

1-Bromo-2-hydroxy-3,3-dimethylbutane.-This was prepared by the method of Guss and Rosenthall,²⁰ by stirring 3,3-dimethylbut-1-ene with N-bromosuccinimide, water, and ether in a flask fitted with an iced-water cooled condenser. The mixture was heated under reflux for 1.5 hr. then stirred overnight at room temperature. The oily bottom layer was separated, dried, and distilled to give 1-bromo-2-hydroxy-3,3-dimethylbutane, b.p. 66°/6 mm. (bath 96°), $n_{\rm D}^{20}$ 1·4801 (lit., ²¹ b.p. 45—46°/4 mm., $n_{\rm D}^{23}$ 1·4683); $v_{\rm max}$ (film) 3350s, 2940s, 1465s, 1455s, 1390m, 1360s, 1255m, 1245m, 1155m, 1080s, 1050s, 947m, and 912m cm.⁻¹; n.m.r. (see above) indicated that small amounts of impurities were present,[†] but they did not hinder the assignment of transitions, although the intensity of one line is affected (Figure 6).

2,2-Dimethylpentan-3-ol.-This was prepared from propionaldehyde and t-butylmagnesium chloride in the normal manner; b.p. 134.5°, $n_{\rm p}^{20}$ 1.4219 (lit.,²² b.p. 133–4°/732 mm., n_D^{20} 1.4223); ν_{max} (film) 3400s, 2950s, 2855s, 1470m, 1395m, 1370m, 1100s, 1060m, and 975s cm.⁻¹.

We thank Dr. S. Sternhell (University of Sydney) for discussions.

[8/1889 Received, December 20th, 1968]

¹⁹ K. A. Oglobin, V. N. Kalikhevich, A. A. Potekin, and V. P. Semenov, Zhur. obshchei Khim., 1964, 34, 1227 (Chem. Abs., 1964, 61, 2967d).
 ²⁰ C. O. Guss and R. Rosenthall, J. Amer. Chem. Soc., 1955,

- 77, 2549.
- S. J. Hurst and J. M. Bruce, J. Chem. Soc., 1963, 1321.
 F. C. Whitmore, R. E. Meter, G. W. Pedlow, and A. H. Popkin, J. Amer. Chem. Soc., 1938, 60, 2788.