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CONFIGURATIONAL ASSIGNMENT OF SECONDARY METHYL GROUPS BASED ON THE AVERAGE COUPLING CONSTANT $\bar{J}$ (CH_3 - CH)

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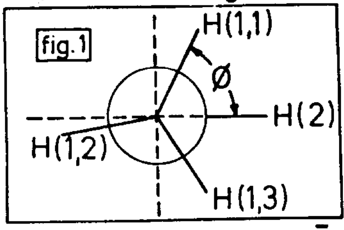
A large series of isomeric molecules differing in the configuration of sec. methyl groups of the same C-atom and showing differences in $\bar{J}(CH_3\text{-}CH)$ (further indicated only with $\bar{J}_3$) of the order 0-1 Hz has already been described in the literature. Some typical examples are listed in Table 1 (1-8). It will be shown that this variability of $\bar{J}_3$'s can be simply discussed on the classical basis using δ-function potential wells (9).



For a given temperature T the time-average value $\bar{J}_3(T)$ of three vicinal coupling constants $J(H_{1,i}, H_2) = J(\emptyset_i)$ ($\emptyset_i \equiv \sphericalangle H(1,i)\text{-}C(1)\text{-}C(2)\text{-}H(2)$; $i=1,2,3$; $\emptyset_i = \emptyset + 2/3\pi(i-1)$) (cf. Fig. 1) can be expressed as :

$$\bar{J}_3(T) = \int_0^{2\pi} J_3(\emptyset)\ p_3\left[G(\emptyset), T\right] d\emptyset = \frac{\int_0^{2\pi} J_3(\emptyset)\ \exp\left[-G(\emptyset)/RT\right] d\emptyset}{\int_0^{2\pi} \exp\left[-G(\emptyset)/RT\right] d\emptyset} \qquad (1)$$

where $\emptyset$ is the angle defined in Fig. 1, p_3 is the temperature-dependent three-fold symmetrical probability distribution (10) expressed approximately via the potential function $G(\emptyset)$ (cf.ref.9), and $J_3(\emptyset)$ is the angular dependence of the group coupling constant J_3 which reflects the fact that the methyl group cannot be freezed out at the position $\emptyset$ with the one two-proton vicinal coupling constant $J(\emptyset)$ (cf. ref. 10,11). As was shown (10), the condition $\delta\bar{J}_3/\delta T \neq 0$ requires to use $J(\emptyset)$ at least in the form

$$J(\emptyset) = A + B\cos\emptyset + C\cos 2\emptyset + D\cos 3\emptyset \qquad (2)$$

which allows to define $J_3(\emptyset)$ (cf. ref. 11) as :

$$J_3(\emptyset) = \frac{1}{3}\sum_{i=1}^{3} J(\emptyset_i) = A + D\cos 3\emptyset\ . \qquad (3)$$

Thus, the eq. (2) allows to distinguish between the values $J_3(\emptyset_s) = J_s$ (staggered form, $\emptyset_s = \pi/3(2i+1)$) and $J_3(\emptyset_s) = J_e$ (eclipsed form, $\emptyset_e = 2/3\pi(i-1)$) which necessitates to introduce the δ-function potential wells in the form $G(\emptyset) = G_s, G_e$ if $\emptyset = \emptyset_s, \emptyset_e$ and $G(\emptyset) = 0$ if $\emptyset \neq \emptyset_s, \emptyset_e$ into eq. (1). Then it follows :

$$\bar{J}_3(T) = A + \overline{D\cos 3\emptyset} = J_s + (J_e - J_s)\left[1 + \exp(\Delta G/RT)\right]^{-1} = J_s + a\ .\ f(\Delta G, T) \qquad (4)$$

where $a = J_e - J_s = 2D$ and $\Delta G = G_s - G_e$.

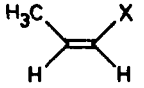
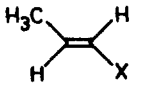
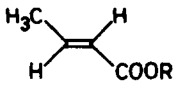
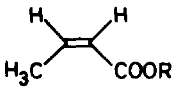
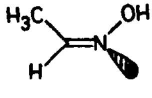
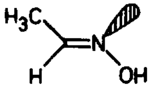
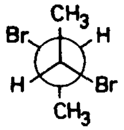
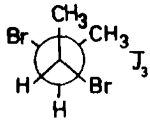
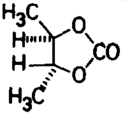
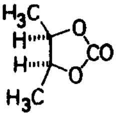
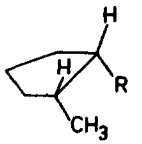
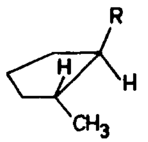
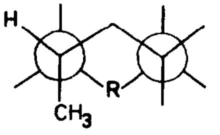
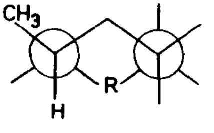
Now, assuming the positive sign of $J(\phi)$ for ϕ_s,ϕ_e and the relations $J_t > J_c$ and $(J_t - J_c) > 2(J_{sc} - J_{ac})$ (definitions: t-trans, c-cis, sc-synclinal, ac - anticlinal) the positive signs of A and C and negative signs of B and D result from eq. (2) (on the contrary to ref. 10) in accordance with sign-alternation predicted theoretically by Karplus (12). Then the sign of $\delta\bar{J}_3/\delta T$ is unambiguously defined by the sign of ΔG (positiv for $\Delta G > 0$ and negativ for $\Delta G < 0$).

Considering now two molecules I and II differing only in the configuration of sec. methyl groups and assuming A(I) = A(II) and D(I) = D(II) we can define the differences between $\bar{J}_3(I)$ and $\bar{J}_3(II)$ measured at the same temperature T using eq. (4) as :

$$\Delta\bar{J}_3(I,II) = \bar{J}_3(I) - \bar{J}_3(II) = |a| \left[f(II) - f(I)\right]. \qquad (5)$$

The dependence of $\Delta\bar{J}_3(I,II)$ on $\Delta G(II)$, choosing $\Delta G(I)$ constant, for the ranges $\pm$ 3 kcal.mol^{-1}, T = 300°K and $|a|$ = 1 Hz (D = -0.5 Hz) is shown in Fig. 2 which allows to deduce the sign of $\Delta\bar{J}_3$ (I,II) for any combinations of signs of $\Delta G(I)$ and $\Delta G(II)$. For the majority of sec. methyl groups bound to sp^3- or sp^2-C-atom it can be supposed that the staggered conformation is <u>a priori</u> more stable in both configurations, i.e. $\Delta G(I) < 0$ and $\Delta G(II) < 0$. For this case the dependence of $\Delta\bar{J}_3(I,II)$ on $\Delta G(II) = \Delta G(I) + k$, choosing $\Delta G(I)$ = = -1 kcal.mol^{-1} and k in the range $\pm$ 1 kcal.mol^{-1}, taking $|a|$ = 1,3 and 5 Hz is shown in Fig. 3. Considering the fragment of the $H_3C(1)-C(2)H-C(3)-R$ type, then the relative stabilities $|\Delta G(I)|$ and $|\Delta G(II)|$ can be estimated primarily from the point of view of hyperconjugation of vicinal

Table 1

 X: H, I, Br, Cl, F J_3 6.4 6.5 6.5 6.6 7.0  J_3 6.4 6.8 6.8 6.9 7.0 [1,2]	 R: H, CH$_3$ J_3 6.7 6.85  R: H, CH$_3$ J_3 7.5 7.27 [2,3]
 $J_3(-30°)$ 5.56 $J_3(90°)$ 5.50 $\frac{\partial J_3}{\partial T} < 0$  $J_3(-30°)$ 6.00 $J_3(90°)$ 5.86 $\frac{\partial J_3}{\partial T} < 0$ [4]	$J_3$6.6   $J_3$6.7  $J_3$6.10  $J_3$6.55 [5]
  $J_3(R,CH_3\text{-cis}) > J_3(R,CH_3\text{-trans})$ [6,7]	  J_3(axial) > J_3(equatorial) [6,8]

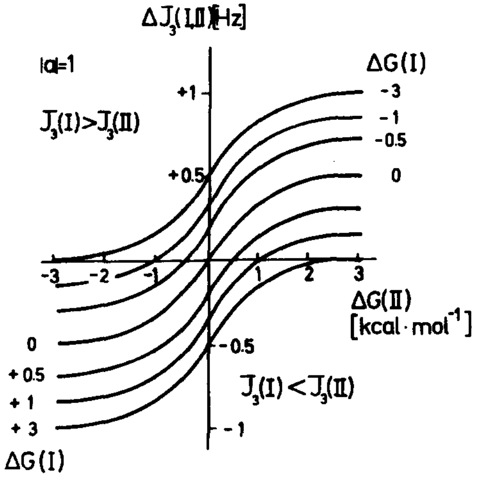


fig.2

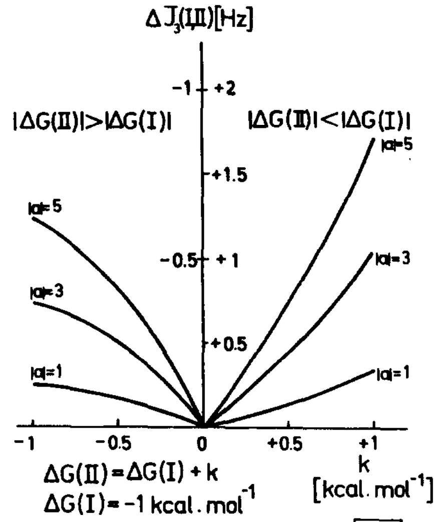


fig.3

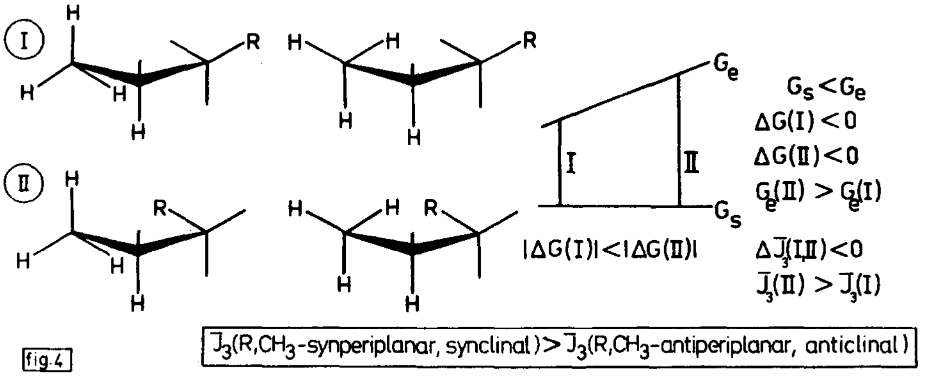


fig.4

J_3(R,CH$_3$-synperiplanar, synclinal) > J_3(R,CH$_3$-antiperiplanar, anticlinal)

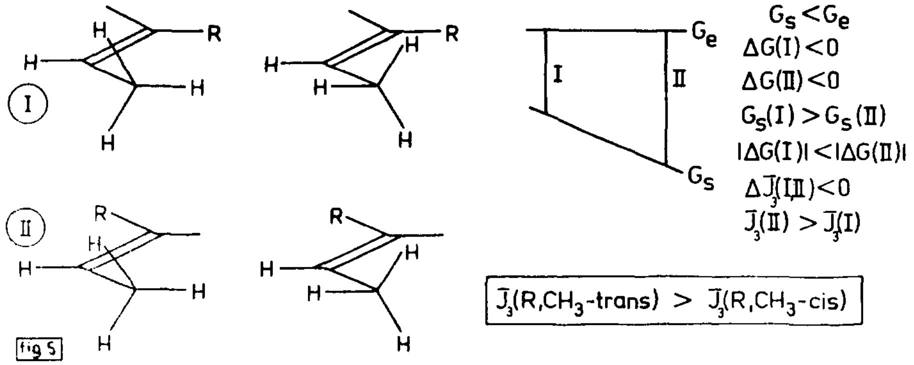


fig.5

J_3(R,CH$_3$-trans) > J_3(R,CH$_3$-cis) orbitals (repulsions of the C(1)-C(2)- and C(3)-R-bonds) and of non-bonding repulsions C(1)-H and R. Assuming that for vicinal sp^3- and sp^2-orbitals their stable configuration is anti, similarly as in the ethane (13) then the dependence of G(∅) on the dihedral angle $\alpha \equiv \sphericalangle C(1)-C(2)-C(3)-R$ for both effects will have maxima at $\alpha = 0^{\circ}$ (R, CH_3-synperiplanar) and minima at $\alpha = 180^{\circ}$ (R, CH_3-antiperiplanar). The corresponding generalised rules for $\Delta \bar{J}_3(I,II)$ derived using Fig. 3 are schematically represented in Fig. 4 and 5. These rules agree well with the majority of cases in Table 1. A typical exception are cis- and trans-isomers of β-methylacrylic acid where the situation is complicated by cis-trans isomerism of C=C-C=O (14).

The consistent interpretation of the cases of Table 1 based on eq. (5) suggests that the sign of $\Delta \bar{J}_3(I,II)$ might be determined primarily by the perturbation of the internal motion of sec. methyl groups. However, the observed effects are very small and their interpretation should be based on the study of model compounds and on the variation of experimental conditions. This should show the role of the steric effects on the one hand, and eliminate the second-order effects on the other hand. Then these effects, if observed, can be utilised with advantage for configurational analyzes of sec. methyl groups even in the case of complex molecules and within the framework of first-order analysis, if both isomers are known (14).

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(11) It can be easily shown, that both eq. (2) and eq. (3) lead to eq. (4) (cf. ref. 10,14). However, the use of J(∅) on the place of $J_3(\emptyset)$ in the eq. (1) (cf. ref. 9,10) makes the eq. (1) formally incorrect in view of the one-point δ-function potential well, i.e. for $G(\emptyset) = G(\emptyset_i)$ if $\emptyset = \emptyset_i$ and $G(\emptyset) = 0$ if $\emptyset \neq \emptyset_i$.

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(14) More detailed discussion of all particular problems will be a subject of subsequent communications (in Collection Czechoslov. Chem. Commun.).