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Conformational Dependence of the Vicinal ^{1}H,^{1}H Coupling Constant in 1,2:3,4-Diepoxides

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Key Words: 1,2:3,4-diepoxides; conformation; Karplus relationship, ^{1}H,^{1}H coupling constants.

***Abstract:** A survey of all 1,2:3,4-diepoxides, of which X-ray structure analyses and ^{1}H-NMR data have been published, shows that in conformationally rigid systems a* Karplus-*like relationship exists between the torsional angle around the inter-epoxide bond and the corresponding vicinal proton-proton coupling constant.*

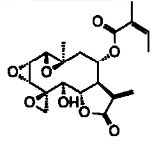
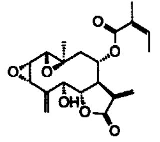
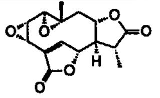
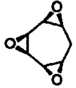
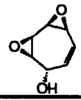
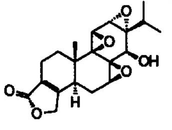
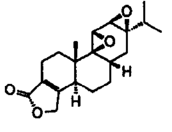
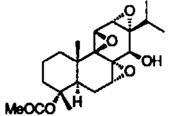
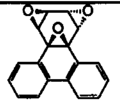
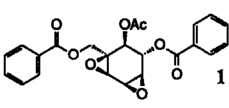
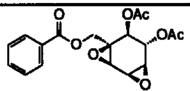
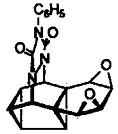
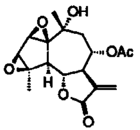
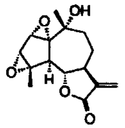
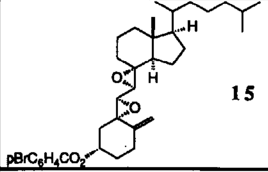
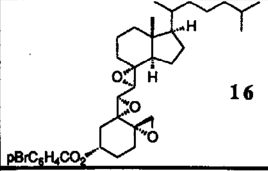
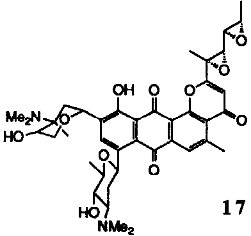
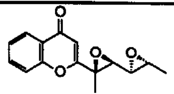
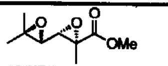
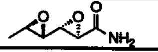
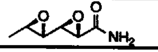
During our work on the conformation of 1,2:3,4-diepoxides[1-3] we tried to get information about the torsional angle around the inter-epoxide bond from a measurement of the vicinal proton-proton coupling constant between the two corresponding protons. However, the original *Karplus* equation[4] is of course not applicable to our case. We therefore sought to derive a similar relationship between dihedral angle and proton-proton coupling constant valid for diepoxides.

All 1,2:3,4-diepoxides, whose crystal structures have been determined by X-ray diffraction and where proton coupling constants have likewise been published, were surveyed. The data are compiled in Table 1[5]. From the compounds **1-11**, which were thought to be more or less conformationally rigid, and which therefore should adopt the same conformation in solution as in the crystal, a *Karplus*-like relationship (equation 1) between the dihedral angle ϕ and the vicinal coupling constant $^3J(^1\mathrm{H},^1\mathrm{H})$ was derived by regression (correlation coefficient $R^2 = 0.934$, standard deviation $\sigma = 0.6$ Hz). The curve corresponding to equation 1 as well as the data points of the epoxides are shown in Figure 1.

$$^3J(^1\mathrm{H},^1\mathrm{H}) = 2.99 - 2.11\cos\phi + 3.05\cos2\phi \qquad (1)$$

Compounds **12-14**, where the diepoxide unit is part of a strained system, do not fit the graph. As was shown earlier[6], the *Karplus* function is not applicable for strained compounds. The 'open-chain' diepoxides **15-22** also do not fit equation 1. This is a clear indication that their conformations in the crystal differ from those in solution. The coupling constants observed in these compounds correspond, however, nicely to the values that are

Table 1. Dihedral angles ϕ and coupling constants $^3J(^1H,^1H)$ of diepoxides.

Compound	ϕ [°]	$^3J(^1H,^1H)$ [Hz] Solvent	Ref.
 **1**	168.9	8.5 $(CD_3)_2CO$	7
 **2**	179.1	8 $(CD_3)_2CO$	7
 **3**	112.1	<0.5 $(CD_3)_2SO$	8
 **4**	36.9 41.4	≤2 ≤2 $CDCl_3$	9
 **5**	34.5	2 $(CD_3)_2CO$	10
 **6**	36.6	3 $CDCl_3$	11
 **7**	16.0	3 $CDCl_3$	12
 **8**	24.4	3 $CDCl_3$	13
 **9**	58.2	1.2 not publ.	14
 **10**	21.9	2.5 $CDCl_3$	15
 **11**	42.9	2.5 $CDCl_3$	15 16
 **12**	3.8	1.1 C_5D_5N	17
 **13**	1.3	1.2 $CDCl_3$	18
 **14**	1.9	1.5 C_5D_5N $(CH_3)_2SO$	19
 **15**	176.0	8 $CDCl_3$	20
 **16**	175.0	5 $CDCl_3$	21
 **17**	30.9	5 $CDCl_3$	22
 **18**	89.4	6 $CDCl_3$	3 23
 **19**	177.1	7.3 $CDCl_3$	2
 **20**	175.2	3.6 $CDCl_3$	1
 **21**	62.7	5.0 $CDCl_3$	1
 **22**	176.6 175.3	4.4 4.4 C_6D_6	24

obtained, when the coupling constants derived from equation 1 for the principal conformations that are present in the solution, are weighted by the respective mole fractions.

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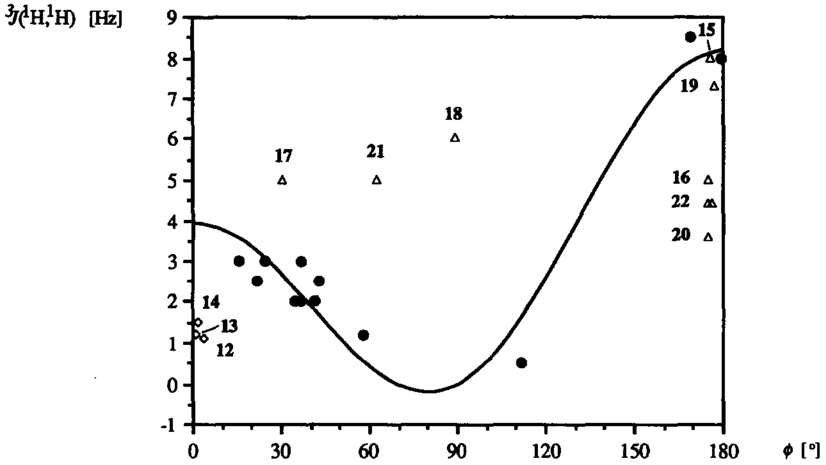

Figure 1. Relationship between the dihedral angle ϕ and the vicinal coupling constant $^3J(^1H,^1H)$ in diepoxides. The curve corresponds to $^3J(^1H,^1H) = 2.99 - 2.11\cos\phi + 3.05\cos2\phi$.

• conformationally rigid diepoxides; ◊ strained diepoxides; Δ 'open-chain' diepoxides.

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5. Most of the dihedral angles were taken from the *Cambridge Data File*; their absolute values are given in Table 1. We thank *Dr. P. S. Manchand* and *Dr. J. Clardy* for providing us with the data of **7** and **13**, respectively.
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