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## THE CHEMICAL SHIFT OF THE $C_2$ PROTONS OF CIS-4,6-DIALKYL-1,3-DIOXANES : A LINEAR RELATION.

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We have measured the chemical shift $\delta_{2e \rightarrow 2a}$ between the equatorial and axial $C_2$ protons of fifteen cis-4,6-dialkyl-1,3-dioxanes (Table I). The compounds may be accepted to exist in anancomeric (3) chair forms, and thus the observed $\delta_{2e \rightarrow 2a}$ variation is not due to multiple conformation presence.

Correlating the $\delta_{2e \rightarrow 2a}$ variation with $\Sigma$Cno, the sum of the number of carbon atoms on the first carbon atom of the $C_4$ and $C_6$ alkyl group, equation (1) is obtained by the method of the least squares (4).

$\delta_{2e \rightarrow 2a} = 17{,}90 + 1{,}170\ \Sigma \mathrm{Cno}$ (in cps) (1) (fig. 1)

r = 0,993 (r is the correlation coefficient between $\delta_{2e \rightarrow 2a}$ and $\Sigma$ Cno) (5)

## TABLE I.

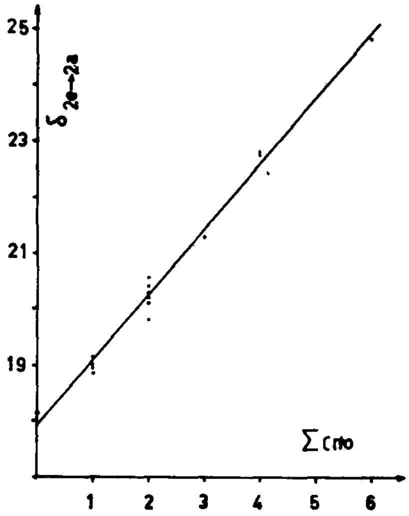
Cis-4,6-dialkyl-1,3-Dioxanes (56.4 Mc).

| $R_4$ | $R_6$ | $\delta_{2e \rightarrow 2a}$ | $\Sigma$Cno | $\Sigma\sigma^*$(a) | Frequency (b) equat. | axial |
|---|---|---|---|---|---|---|
| Me | Me | 18.15 ± 0.2 | 0 | 0.000 | 0 | 0 |
| Me | Et | 19.15 ± 0.1 | 1 | -0.100 | 0 | 1 |
| Me | *n*.Pr | 18.85 ± 0.1 | 1 | -0.115 | 0.5 | 1.3 |
| Me | *n*.Bu | 18.95 ± 0.15 | 1 | -0.130 | 0.6 | 1.5 |
| Me | *i*.Bu | 19.00 ± 0.2 | 1 | -0.125 | 0.5 | 1.5 |
| Me | *i*.Pr | 20.58 ± 0.2 | 2 | -0.190 | -0.8 | 1.6 |
| Me | *sec*.Bu | 20.1 ± 0.3 | 2 | -0.210 | -0.6 | 1.4 |
| Et | Et | 20.44 ± 0.25 | 2 | -0.200 | -1.1 | 1.2 |
| *n*.Pr | *n*.Pr | 20.2 ± 0.15 | 2 | -0.230 | -0.4 | 1.6 |
| *i*.Bu | *i*.Bu | 19.8 ± 0.15 | 2 | -0.250 | -0.3 | 1.5 |
| *n*.Bu | *n*.Bu | 20.3 ± 0.1 | 2 | -0.260 | -0.3 | 2.0 |
| Me | *t*.Bu | 21.20 ± 0.15 | 3 | -0.300 | -2.3 | 0.7 |
| *i*.Pr | *i*.Pr | 22.80 ± 0.1 | 4 | -0.380 | -3.1 | 1.5 |
| *sec*.Bu | *sec*.Bu | 22.75 ± 0.2 | 4 | -0.410 | -2.7 | 1.9 |
| *t*.Bu | *t*.Bu | 24.82 ± 0.15 | 6 | -0.600 | -5.1 | 0.5 |

(a) R.W.Taft, Jr., "Steric Effects in Organic Chemistry" M.S. Newman, Ed., John Wiley & Sons, Inc., New York, 1956, p. 619.

(b) Relative to the corresponding frequency of *cis*-4,6-diMe-1,3-dioxane as zero. Negative sign is downfield shift.

FIG. 1



Correlating the $\delta_{2e\rightarrow 2a}$ variation with $\Sigma\sigma^{*}$, the sum of the inductive $\sigma$ values of the $C_4$ and $C_6$ alkyl groups, a similar equation is obtained. The correlation, however, is not as good as for equation (1). Correlating with both $\Sigma$Cno and $\Sigma\sigma^{*}$, the multiple regression equation (2) is obtained.

$$\delta_{2e\rightarrow 2a} = 18,02 + 1,714\,\Sigma\mathrm{Cno} + 5,664\,\Sigma\sigma^{*}$$

(in cps) (2).

R = 0,995 (R is the multiple correllation coefficient) (5). The standard partial regression coefficients learn that $\Sigma$Cno has more influence in "explaining" $\delta_{2e\rightarrow 2a}$ than $\Sigma\sigma^{*}$. The proportion of the total sum of squares attributable to $\Sigma$Cno alone (eq. 1) is $r^2 = 0,98$. On the other hand the proportion of the total sum of squares attributable to the combined regression on $\Sigma$Cno and $\Sigma\sigma^{*}$ (eq. 2) is $R^2 = 0,99$. The gain in "explained" variability on adding $\Sigma\sigma^{*}$ as a variable, although significant, is so small that, in our opinion, $\Sigma\sigma^{*}$ may be neglected as a second variable. The satisfactory correlation between $\delta_{2e \rightarrow 2a}$ and $\Sigma\sigma^*$ is then only a reflection of the correlation between $\Sigma$Cno and $\Sigma\sigma^*$. Moreover, there are two experimental reasons to prefer $\Sigma$Cno over $\Sigma\sigma^*$ as the significant variable. First it is found that the $\delta_{2e \rightarrow 2a}$ variation is mainly due to a downfield shift of the low field equatiorial $C_2$ proton (Table I). If, however, $\Sigma\sigma^*$ was the important variable, then $\delta_{2e \rightarrow 2a}$ would have changed through increased shielding, resulting in an upfield shift of the $C_2$ protons. Secondly the $\delta_{2e \rightarrow 2a}$ values of some trans (di-equatorial) 4-aryl-5-methyl-1,3-dioxanes have been reported (6). The aryl groups are phenyl, 3-nitrophenyl, 4-chlorophenyl and 4-methoxyphenyl. The $\delta_{2e \rightarrow 2a}$ value is constant in this series (0.39 ppm) and this militates also against the inductive effect being chemically significant.

Even though these considerations indicate that $\Sigma$Cno is the significant variable, it is difficult to provide a theoretical basis for its origin. Recently however a similar phenomenon has been observed in acetates MeCOOR (7). The resonance frequency of the methyl group is influenced not only by the inductive effect of the R group, but also by the number of carbon atoms on the β carbon atom(s) of the group. A steric inhibition of resonance through specific conformation occurrence was advanced as being responsible for the observation (7).

## Experimental.

The PMR spectra were run in carbon disulfide solutions (1 mmol in 0,6 ml solvent) on a VARIAN DP 56,4 Mc spectrometer. The temperature was 28°C ± 1.

## References.

(1) Paper VII, Tetr. Letters, **38**, 4579 (1966).

(2) Aspirant of the "Nationaal Fonds voor Wetenschappelijk Onderzoek".

(3) For a definition of this term, see M. Anteunis, D. Tavernier & F. Borremans, Bull.Soc.Chim.Belges **75**, 396 (1966).

(4) Prof. Dr. C. C. Grosjean, Director of the Computing Laboratory of the University of Ghent is thanked for calculations.

(5) G.W. Snedecor, Statistical Methods, 5th ed. The Iowa State College Press.

(6) J. Delmau; Thesis (1965) Lyon - France.

(7) O.Rosado-Lojo, C. Kinney Hancock, A. Danti; J.Org.Chem. **31** 1899 (1966).

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