Acta Chemica Scandinavica B 37 (1983) 289–296

Conformational Analysis. XXIII. ^{13}C and ^{1}H NMR Conformational Study of 2-Oxo-1,3-dioxane and Its Methyl Derivatives

KALEVI PIHLAJA * and KYLLIKKI ROSSI

Laboratories for Organic and Physical Chemistry, University of Turku, SF-20500 Turku 50, Finland

The ^{13}C NMR chemical shifts for 2-oxo-1,3-dioxane and its methyl derivatives are reported. Substituent effects on them are derived and their type and magnitude shown to be closely related to the exact ring geometry and other conformational aspects. Together with some ^{1}H NMR data the results point out the usefulness of the ^{13}C NMR chemical shifts in conformational and configurational analysis.

Relatively little attention has been previously paid to the conformational analysis of 2-oxo-1,3-dioxane (*1*) and its methyl derivatives (*2–24*). Since the early work of Arbuzov *et al.*[1,2] Katzhendler *et al.*[3] have studied the ^{1}H NMR spectra of a few 2-oxo-1,3-dioxanes and explained them in favour of a predominant chair form. Pihlaja and coworkers [4] concluded from the ^{1}H NMR spectra of *1*, *5–7*, and *10* (Table 1) that they exist in a chair conformation where the $C_{4\text{-}5\text{-}6}$ region of the ring is flattened when compared with cyclohexanes but more puckered than that of the 1,3-dioxane ring. Using the values of the vicinal coupling constants they estimated [4] that *r*-4,*cis*-5,*trans*-6-trimethyl-2-oxo-1,3-dioxane (*14*) contains about 58 % of the 5-equatorial (eea) conformer. Also Hellier and Webb [5] note that substituted derivatives of *1* prefer the chair form and Samitov and Aminov [6] state that *2* is predominantly in the equatorial chair form.

In the present work we report the ^{13}C NMR chemical shifts for 2-oxo-1,3-dioxane (*1*) and all of its methyl derivatives (Table 2). From them the substituent effects on the ring carbon atoms are estimated to clarify the ring conformation and possible conformational equilibria in detail.[7] To get further insight into compounds with possible conformational equilibria the ^{1}H NMR spectra of *2*, *3* and *14* were also recorded and analyzed.

EXPERIMENTAL

The 2-oxo-1,3-dioxanes were prepared by the method described before.[4] Their boiling or melting points and refractive indices are presented in Table 1. The ^{1}H NMR spectra of *2* and *3* were recorded on a Jeol FX-200 and that of *14* on a Bruker 360 MHz NMR spectrometer using $CDCl_3$ as solvent (Table 6). The spectrum of *2* was analyzed using a LAME program whereas the spectra of *3* and *14* were practically first order at 200 and 360 MHz, respectively.

RESULTS

The ^{13}C chemical shift data for compounds *1–24* are collected in Table 2 along with the corresponding assignments. The chemical shift parameters (Table 3–5) were derived by a multiple linear regression analysis of the shift data using eqn. (1),[7–9]

$$\delta C(x) = \delta_p C(x) + \Sigma SE(x) \qquad (1)$$

where $\delta C(x)$ is the chemical shift of the xth carbon in any given derivative, $\delta_p C(x)$ that of the

* To whom correspondence should be addressed.

0302-4369/83 $02.50
© 1983 Acta Chemica Scandinavica

Table 1. 2-Oxo-1,3-dioxanes prepared in this study.

	2-Oxo-1,3-dioxane	B.p./K kPa^{-1} or M.p./K	n_d^{293}
1	Parent	314	
2	4-Me	436/2.3	1.4453
3	5-Me (24 % a+76 % e)	363–364/0.1	1.4492
4	4,4-Me_2	348	
5	5,5-Me_2	370	
6	*cis*-4,6-Me_2	435/2.8	1.4413
7	*trans*-4,6-Me_2	432–433/2.8	1.4459
8	*trans*-4,5-Me_2	422–428/1.5 [a]	1.4417 [a]
9	*cis*-4,5-Me_2 (5 % ae+95 % ea)		
10	4,4,6-Me_3	369	
11	*r*-4,*cis*-5,*trans*-6-Me_3 (33 % aae+67 % eea)	429/1.7	1.4451
12	*r*-4,*trans*-5,*cis*-6-Me_3	431/1.9	1.4476 [b]
13	*r*-4,*cis*-5,*cis*-6-Me_3		
14	4,4,5-Me_3 (12 % 5a+88 % 5e)	327	
15	4,5,5-Me_3	364	
16	4,4,5,5-Me_4	458	
17	4,4,6,6-Me_4	351	
18	*cis*-4,5,5,6-Me_4	331 [c]	
19	*trans*-4,5,5,6-Me_4		
20	*trans*-4,4,5,6-Me_4	376 [d]	
21	*cis*-4,4,5,6-Me_4		
22	4,4,5,6,6-Me_5	341	
23	4,4,5,5,6-Me_5	376	
24	4,4,5,5,6,6-Me_6	441	

[a] For a mixture of *8* and *9*. [b] For a mixture of *12* and *13*. [c] For a mixture of *18* and *19*. [d] For a mixture of *20* and *21*.

same carbon atom in the parent compound (*1*) and $\Sigma SE(x)$ the sum of the different substituent effects influencing it.[7–9] The chemical shift parameters were first calculated using the shift data for compounds *1, 2, 4–8, 10, 12, 13, 15, 16, 18–21,* and *23* with anancomeric or two equivalent chair conformations. The values of the shift parameters so obtained were then used to estimate the mol fractions of the two unequal chair conformations in the case of compounds *3, 9, 11,* and *14* (Scheme 1). We also came up with numerically the same parameters before and after including the shift data for compounds *3, 9, 11* and *14* weighed by the best fit values of the mol fractions (Scheme 1).

Compound *2*, however, seems to be predominantly in the equatorial chair form as can be concluded also from its ^{1}H NMR spectrum (Table 6). The data for compounds *17, 22* and *24* were not used for deriving the chemical shift parameters (Tables 3–5) since they are the only compounds with independent 4a6a, 4a5e6a, and 4a5a6a substitution patterns, respectively.

PARAMETRIZATION

In addition to the primary (α, β, γ, δ), geminal (G_i), and vicinal (ee, ea, ae; Tables 3–5) effects we have introduced some long range and polysubstitution ($n \geqq 3$) parameters to explain further perturbation of the basic ring geometry for reasons stated before.[7,8]

The long range and polysubstitution parameters are considered significant if they are larger than 0.2 ppm and/or at least twice their standard deviations. All substituent effects which have been involved in the multiple linear regression analysis are present at least three times (Tables 3–5). Of course, it can be argued that given enough parameters a given set of data can be made to fit a pattern but we feel, however, that this is not possible without forgetting the chemistry behind our experiments. Our conclusion is drawn from the observation that independent of the initial parametrization we always ended up with the same set of best parameters. Furth-

Table 2. ^{13}C chemical shifts of 2-oxo-1,3-dioxanes.

	2-Oxo-1,3-dioxane	C-2	C-4	C-5	C-6	Methyl carbons
1	Parent	148.66	68.09	21.70	68.09	
2	4-Me	149.18	75.95	28.52	67.18	21.05(4e)
3	5-Me (24 % a+76 % e)	148.72	73.29	26.18	73.29	11.83(5e) [a]
4	4,4-Me_2	149.18	81.35	32.68	64.84	27.74(av.)
5	5,5-Me_2	148.20	77.45	28.33	77.45	20.92(av.)
6	*cis*-4,6-Me_2	149.44	75.37	36.38	75.37	21.12(4/6e)
6	*trans*-4,6-Me_2	149.57	72.70	33.79	72.70	20.79(4/6av.)
8	*trans*-4,5-Me_2	148.92	81.27	32.83	72.26	19.23(4e), 11.95(5e)
9	*cis*-4,5-Me_2 (5 % ae+95 % ea)	149.16	78.09	29.57	72.61	16.99(4e), 9.89(5a) [a]
10	4,4,6-Me_3	149.50	80.89	40.48	72.32	29.89(4e), 26.51(4a), 21.12(6e)
11	*r*-4,*cis*-5,*trans*-6-Me_3 (33 % aae+67 % eea)	149.22	76.37	35.72	78.03	19.86(4e), 11.94(5a), 15.90(6a) [a]
12	*r*-4,*trans*-5,*cis*-6-Me_3	149.24	80.24	39.78	80.24	19.18(4/6e), 12.33(5e)
13	*r*-4,*cis*-5,*cis*-6-Me_3	149.24	79.01	34.24	79.01	19.88(4/6e), 3.78(5a)
14	4,4,5-Me_3 (12 % 5a+88 % 5e)	149.18	84.53	35.28	70.11	27.61(4e), 21.31(4a), 11.31(5e) [a]
15	4,5,5-Me_3	148.79	82.91	31.25	77.77	15.27(4e), 21.18(5e), 16.83(5a)
16	4,4,5,5-Me_4	148.92	86.61	33.72	75.69	23.78(4av.), 20.66(5av.)
17	4,4,6,6-Me_4	150.48	80.57	44.77	80.57	29.69(4/6av.)
18	*cis*-4,5,5,6-Me_4	148.98	83.37	34.44	83.37	14.77(4/6e), 20.89(5e), 11.06(5a)
19	*trans*-4,5,5,6-Me_4	148.92	80.96	33.72	80.96	15.79(4/6av.), 20.34(5av.)
20	*trans*-4,4,5,6-Me_4	149.18	84.14	42.56	77.18	27.74(4e), 21.37(4a), 11.95(5e), 19.62(6e)
21	*cis*-4,4,5,6-Me_4	149.44	83.69	38.07	74.59	28.39(4e), 26.57(4a), 7.15(5a), 18.06(6e)
22	4,4,5,6,6-Me_5	149.96	84.34	45.94	84.34	30.41(4/6e), 22.55(4/6a), 11.89(5e)
23	4,4,5,5,6-Me_5	149.11	86.74	36.58	79.01	24.04(4e), 23.39(4a), 20.40(5e), 14.68(5a), 16.27(6e)
24	4,4,5,5,6,6-Me_6	150.02	87.19	40.41	87.19	26.77(4/6av.), 21.18(5av.)

[a] The more favoured orientation shown in parentheses.

ermore, the possible interdependence of the different substituent effects was carefully checked to minimize their total number.

DISCUSSION

Shift Parameters

α-effects. In the case of C(4/6) both the axial and equatorial α-effects are larger than those of 1,3-dioxanes (5.37 *vs.* 0.95 and 7.83 *vs.* 5.76, respectively). This is indicative for the different chair conformations since the carbonate moiety is planar in 2-oxo-1,3-dioxanes which has both through-frame and through-space influence on their geometry and hence on the magnitude of the shift effects in them.

At C(5) the axial and equatorial α-effects are very close to each other both in 1,3-dioxanes and in their 2-oxo derivatives ($\alpha_e-\alpha_a$=0.26 and –0.13, respectively) although they are about 1 ppm more deshielding in the latter ring system. It is also very interesting to note that the geminal α-effect (G_α) at C(4/6) of (*1*) is zero whereas that of 1,3-dioxanes is –2.60 ppm. This is strong evidence for the importance of the presence or lack of interacting synaxial hydrogen atoms. At C(5) G_α equals –2.35 ppm in *1* and –2.57 ppm in 1,3-dioxanes.

β-effects. $\beta_e-\beta_a$ at C(4/6) is almost the same for *1* and for 1,3-dioxanes [8a] (Table 3) although in the former ring system both β-effects are *ca.* 1 ppm less deshielding. Even in 1,3-oxathianes [11] and 1,3-dithianes [12] $\beta_e-\beta_a$ at C(4/6) has a value which is very close to those in the above compounds.

At C(5) (Table 4) $\beta_e-\beta_a$ is only 1.4 ppm for *1* whereas in the other compounds mentioned

Table 3. Parameters for shifts at C(4/6).

The source of the substituent effects	Parameters/ppm [a]		No. of occurrences
4e	α_e	7.83±0.07	23
4a	α_a	5.37±0.08	12
5e	β_e	5.41±0.09	21
5a	β_a	4.01±0.12	19
6e	γ_e	-0.91±0.08	23
6a	γ_a	-2.29±0.11	12
4e5a	$\alpha_e\beta_a$	-1.89±0.12	12
5a6e	$\beta_a\gamma_e$	1.59±0.11	12
5e6e	$\beta_e\gamma_e$	-0.46±0.11	12
4e6e	$\alpha_e\gamma_e$	0.39±0.09	12
4e6a	$\alpha_e\gamma_a$	-0.79±0.12	8
4e4a5e	$\alpha_e\alpha_a\beta_e$	-1.90±0.11	4
4e5a6a	$\alpha_e\beta_a\gamma_a$	-0.80±0.13	4
4e5e5a	$\alpha_e\beta_e\beta_a$	-0.63±0.10	6
4a5a6e	$\alpha_a\beta_a\gamma_e$	-0.72±0.12	6
4a5e6e	$\alpha_a\beta_e\gamma_e$	0.22±0.12	4
4a5e5a	$\alpha_a\beta_e\beta_a$	0.34±0.14	3
5e6e6a	$\beta_e\gamma_e\gamma_a$	0.21±0.11	4

[a] rms 0.110 ppm, av.diff. ±0.06 ppm, range 21.90 ppm.

Table 4. Parameters for shifts at C(5).

The source of the substituent effects	Parameters/ppm [a]		No. of occurrences
4e	β_e	6.75±0.06	26
4a	β_a	5.39±0.11	11
5e	α_e	4.39±0.08	13
5a	α_a	4.52±0.20	12
4,4	G_β	-1.21±0.12	7
5,5	G_α	-2.32±0.23	6
4e5a	$\alpha_a\beta_e$	-3.32±0.14	14
4a5e	$\alpha_e\beta_a$	-2.19±0.18	7
4e6e	$\beta_e^4\beta_e^6$	1.16±0.13	8
4e5e6e	$\alpha_e\beta_e^4\beta_e^6$	-0.93±0.12	4
4a5e5a	$\alpha_e\alpha_a\beta_a$	-0.33±0.14	4
4e4a5e	$\alpha_e\beta_e\beta_a$	0.76±0.19	4
4e5e5a	$\alpha_e\alpha_a\beta_e$	-0.46±0.15	7
4e5a6a	$\alpha_a\beta_e^4\beta_e^6$	-0.33±0.12	4

[a] rms 0.097 ppm, av.diff. ±0.04 ppm, range 13.60 ppm.

above it varies from 3.0 to 3.5 ppm. This resembles the situation with the α_e–α_a difference discussed above and shows again that the spatial and electronic environment at C(4/6) of *1* differs clearly from that of, *e.g.*, 1,3-dioxane because of the influence of the 2-oxo group. Also the geminal β-effects of *1* and 1,3-dioxane are somewhat different (Tables 3 and 4).[8a]

γ-effects. The effect of the carbonate moiety is clearly seen also in the γ-effects. At C(2) both γ_e and γ_a are small and deshielding whereas in 1,3-dioxanes they are both deshielding and γ_a has

Table 5. Parameters for shifts at C(2).

The source of the substituent effects	Parameters/ppm [a]		No. of occurrences
4e	γ_e	0.46±0.05	26
4a	γ_a	0.36±0.08	11
5a	δ_a	0.20±0.16	12
4,4	G_γ	–0.21±0.07	7
5,5	G_δ	–0.62±0.17	6
4e6e	$\gamma_e^4\gamma_e^6$	–0.17±0.08	8
4e5e	$\gamma_e\delta_e$	–0.11±0.04	14
4e5a	$\gamma_e\delta_a$	–0.17±0.10	14
4e5e5a	$\gamma_e\delta_e\delta_a$	0.33±0.11	7
4a5e6e	$\gamma_a\gamma_e\delta_e$	–0.16±0.07	4

[a] rms 0.077 ppm, av.diff. ±0.05 ppm, range 1.37 ppm.

got a normal value of –7.1 ppm (Table 5). At C(4/6) γ_e is not much different from that in 1,3-dioxanes whereas the γ_a-effect at C(4/6) in *1* is much less shielding than in 1,3-dioxanes (–2.34 *vs.* –4.72 ppm). This is mainly due to the lack of a synaxial hydrogen atom (γ-H) at C(2) and to a lesser extent to the planarity of the carbonate grouping[13] as shown by the ratio of the effects in *1* and 1,3-dioxane (~0.5).

δ-effects. These effects are, in general, small. From the two possible δ-effects in *1* only δ_a at C(2) has a small nonzero value (Table 5).

Vicinal and related polysubstitution effects. In our recent report on 1,3-dioxanes [7] we pointed out that in addition to vicinal effects $\alpha_e\beta_e$,$\alpha_e\beta_a$, $\alpha_a\beta_e$, $\beta_e\gamma_a$, and $\beta_a\gamma_e$ [9] one should take into account their combined influences since, for instance, the real effect of $\alpha_e\beta_a\gamma_e$ substitution can differ significantly from the values of $\alpha_e\beta_a+\beta_a\gamma_e$. This is also the case in 2-oxo-1,3-dioxanes which again lends support to the postulation that vicinal polysubstitution ($n\geq3$) has a further perturbation effect on the basic ring geometry. Comparison of the different $\alpha\beta$ shifts at C(4/6) of 2-oxo-1,3-dioxanes with the corresponding shifts in 1,3-dioxanes[8a] (Tables 3 and 4) shows clearly the influence of the carbonaate moiety. Especially different are $\alpha_a\beta_e$ effects at C(4/6) and $\alpha_e\beta_a$ effects at C(5). As to the polysubstitution effects both their type and magnitude are different in the carbonates and 1,3-dioxanes themselves (Tables 3–5).[7,8a] The fundamental difference in the α_{ae} effects between 2-oxo-1,3-dioxanes and 1,3-dioxanes reflects again the difference in geometries and hence the difference in steric interactions.

Buttressing and syn-*axial effects.* There are three such influence at C(4/6) namely $\alpha_e\gamma_e$, $\alpha_e\gamma_a$, and $\alpha_a\gamma_a$ which all have numerical values very close to those of 1,3-dioxanes. At C(5) the $\beta_e^4\beta_e^6$ effect, 1.16 ppm, is greatly enhanced in comparison with that of 1,3-dioxanes, 0.37 ppm (Table 4).[8a] A fundamental difference iis seen also in the δ-synaxial effects at C(5) since $\beta_a^4\beta_a^6$ is 0.05 ppm (Table 7) in 2-oxo-1,3-dioxanes but –1.02 ppm in 1,3-dioxanes. In general, the similarities and differences in the substituent effects of 2-oxo-1,3-dioxanes and 1,3-dioxanes reflect the magnitudes of their molecular interactions and the basic deviations in their geometries.

Chair–Chair Equilibria and ^{1}H NMR Spectra

4-Methyl-2-oxo-1,3-dioxane (*2*) attains exclusively the equatorial chair form the predominance of which can be concluded from the ^{1}H NMR parameters and is confirmed by the substituent effects on the ^{13}C chemical shifts. We can now use the values of the vicinal coupling constants (Table 6) to evaluate the position of the chair–chair equilibria in *3*, *11* and *14* in order to compare the results with those from the ^{13}C shift data below.

For 5-methyl-2-oxo-1,3-dioxane (*3*) we take the model values from the ^{1}H spectrum of *2*, namely J_{aa} 11.5 and J_{ee} 2.9 Hz. The latter value will be used for the three other compounds, too. The model values for the ea and ae couplings are more difficult to define and hence we do not use

Table 6. ^{1}H NMR parameters of 4-methyl- (*2*), 5-methyl- (*3*) and 4,4,5-trimethyl-2-oxo-1,3-dioxanes (*14*). Solvent $CDCl_3$, internal standard TMS.

Compound	Proton	δ/ppm	J/Hz	
2 [a]	5a	1.93	5a5e	−14.41; 6a6e −11.03
	5e	2.10	5a6a	11.54; 5e6a 3.56
	6a	4.39	5e6e	2.92; 5a6e 5.02
	6e	4.44	4a5e	3.38; 4a5a 10.27
	4a	4.63	4a,CH_3	6.35
	CH_3	1.44		
3 [a,b]	5a	2.38 [2.39] [c]	44	−10.7 [−10.7]; 5a, CH_3 6.8 [6.8]
	4/6a	4.11 [4.09]	45(t)	9.2 [9.2]
	4/6e	4.42 [4.40]	45(c)	4.5 [4.6]
	CH_3	1.05 [1.05]	'4e6e'	1.0 [1.0]; '4a6a' ~0.4
14 [d]	5a	2.19	6e6a	−11.0
	6a	4.11	5a6a	10.85
	6e	4.30	5a6e	5.0
	CH_3(5)	1.00	5a,CH_3	7.0
	CH_3(4a)	1.37		
	CH_3(4e)	1.47		

[a] Jeol FX-200. [b] About 73:27 mixture of the equatorial and axial chair forms (see the text). [c] The values in the brackets obtained on a Jeol PFT-100. [d] About 86:14 mixture of the 5-equatorial and 5-axial chair forms (see the text); Bruker WM 360.

them for our calculations. Consequently, we obtain eqn. (2),

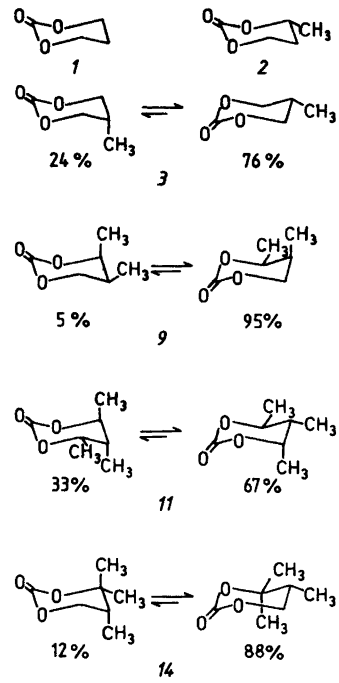
$$9.2 = X_{5e} \cdot 11.5 + (1-X_{5e})2.9 \quad (2)$$

from which $X_{5e}=0.73$. This is in excellent agreement with the result, 0.76, given by the ^{13}C chemical shift correlation taking into account that the error limits are about 0.03 in both calculations. If we assume that the actual value of $J_{4a6a}\sim 0$ as usual we obtain $J_{4e6e}\sim 1.4$ Hz a value which gives 'J_{4a6a}'$=0.27\times 1.4=0.4$ Hz and 'J_{4e6e}'$=0.73\times 1.4=1.0$ Hz in good agreement with the experimental finding (Table 6).

In the case of *r*-4,*cis*-5,*trans*-6-trimethyl derivative (*11*) the weighted average of the J_{aa} and J_{ee} type couplings is 7.8 Hz.[4] In our previous report [4] we did not have a good enough selection of model values. Hence we now reestimate the conformer ratio of *11* using $J_{aa}=10.3$ Hz and $J_{ee}=2.9$ Hz obtained from *2* as models [eqn. (3)].

$$7.8 = X_{aee} \cdot 10.3 + (1-X_{aee})2.9 \quad (3)$$

This leads to $X_{aee}=0.66$ which is not far from the earlier estimate [4] ($X_{aee}=0.58$) and is again



Scheme 1.

practically equal to the result (X_{aee}=0.67) from the ^{13}C chemical shift correlation (Scheme 1).

Finally we calculate the conformer population of *14* (Scheme 1) using J_{aa}=12.1 Hz which has been taken from 4,4,6-trimethyl-2-oxo-1,3-dioxane [4] and J_{ee}=2.9 Hz as above [eqn. (4)].

$$10.85 = X_{5e} \cdot 12.1 + (1 - X_{5e})2.9 \quad (4)$$

Thus the 4,4,5-trimethyl derivative is an 86:14 mixture of the 5e and 5a chair forms, a result which again fits together very well with that obtained from the ^{13}C NMR spectra (Scheme 1).

Chair–Chair Equilibria and the ^{13}C Chemical Shifts

To test the anancomerism of 4-methyl-2-oxo-1,3-dioxane (*2*) we calculated the values of the substituent effects on the ^{13}C chemical shifts using different axial–equatorial conformer ratios. However, we always ended up with the best fit when *2* was taken exclusively equatorial. Since $\Delta_e - \Delta_a$ is relatively small at all of the ring atoms (Tables 3–5) we can only conclude that *2* consists of at least 98 % of the equatorial chair form. The clear predominance of the equatorial conformer is supported also by the observation that the positions of the chair–chair equilibria of *3, 11* and *14* do not deviate significantly from those of the corresponding 1,3-dioxanes [7] (Table 6 and Scheme 1). The conformational energy of an axial 5-methyl group (2.9 kJmol^{-1}, Scheme 1) is somewhat less than that in 1,3-dioxanes and hence we can expect that the ratio of the 4e5a and 4a5e chair forms in *9* is also very close to that in 1,3-dioxanes (97:3).[7] Actually we can easily estimate that the proportion of the 4e5a form should be about 95 %. This estimate fits very well in the multiple linear correlation of the ^{13}C chemical shift data and leads, together with the other data, to the conclusion that the stereochemistry of the C_4–C_5–C_6 moiety of 2-oxo-1,3-dioxanes does not differ fundamentally from that of 1,3-dioxanes.

Finally we will discuss compounds *17, 22* and *24* which include 4a6a, 4a5e6a and 4a5a6a type increments, respectively. The values of these effects have been calculated manually and are shown in Table 7 together with the comparable data for 1,3-dioxanes. The values of the 4a6a effects are fairly close to those of 1,3-dioxanes at all ring atoms although the structural difference is somewhat reflected in the influence at C-5. Also the 4a5e6a effects are very small and almost equal in both sets of compounds whereas the 4a5a6a effects are clearly more deshielding in 1,3-dioxanes. In 2-oxo-1,3-dioxanes the values of the latter effects are quite small in agreement with the chair conformation. *cis*-2,4,4,5,6,6-Hexamethyl-1,3-dioxane has been stated to attain the 1,4-twist form [7] to some extent and this statement finds support both from the magnitude of the 4a5a6a effects and from thermochemical calculations.[8a]

CONCLUSION

A thorough correlation of the ^{13}C NMR chemical shift data with some complementary ^1H NMR results led to a consistent picture of the predominance of the chair conformation and the existence of some chair–chair equilibria in 2-oxo-1,3-dioxanes. Accordingly the present work strongly supports the view [7,8] that ^{13}C chemical shifts, measured at 298 K only, are very useful and sensitive detectors in configurational and conformational analysis. It is obvious that the

Table 7. The values of the substituent effects derived manually from compounds *17, 22* and *24* together with those of 1,3-dioxanes.[8a]

Substituent effect/ppm	Ring carbon atom [a] C-2	C-4/6	C-5
4a6a	+0.77(+0.96)	+2.88(+3.44)	+0.05(−1.02)
4a5e6a	+0.02(−0.21 [b])	+0.29(+0.79 [b])	+0.57(+0.30 [b])
4a5a6a	+0.16(+0.69 [c])	+0.95(+3.18 [c])	+1.15(+3.82 [c])

[a] The values for 1,3-dioxanes in parentheses. [b] Estimated from *trans*-2,4,4,5,6,6-hexamethyl-1,3-dioxane.[7,8a] [c] Estimated from *cis*-2,4,4,5,6,6-hexamethyl-1,3-dioxane.[8a]

more data becomes available the better we can benefit from the application of ^{13}C chemical shifts to solving ring conformations and other structural problems.

REFERENCES

1. Arbuzov, B. A. *Bull. Soc. Chim. Fr.* (1960) 1311.
2. Arbuzov, B. A., Samitov, Yu. Yu. and Mamina, R. M. *Dokl. Akad. Nauk. SSSR 143* (1962) 338.
3. Katzhendler, J., Poles, L. A. and Sarel, S. *Israel J. Chem. 10* (1972) 111.
4. Pihlaja, K., Teinonen, K.-J. and Äyräs, P. *Suom. Kemistil. B 43* (1970) 41.
5. Hellier, D. G. and Webb, F. J. *Org. Magn. Reson. 9* (1977) 347.
6. Samitov, Yu. Yu. and Aminova, R. M. *Zh. Strukt. Khim. 5* (1964) 207.
7. Pihlaja, K. and Nurmi, T. *Israel J. Chem. 20* (1980) 160.
8. a. Pihlaja, K., Kivimäki, M., Myllyniemi, A.-M. and Nurmi, T. *J. Org. Chem. 47* (1982) 4688 and references therein; b. Pihlaja, K. and Nurmi, T. *Finn. Chem. Lett.* (1977) 141; c. Pihlaja, K. and Rossi, K. *Acta Chem. Scand. B 31* (1977) 899; d. Labaziewicz, H., Riddell, F. G. and Sayer, B. G. *J. Chem. Soc. Perkin Trans. 2* (1977) 619.
9. Dalling, D. K. and Grant, D. M. *J. Am. Chem. Soc. 94* (1972) 5318.
10. Pihlaja, K. and Kankare, J. *Acta Chem. Scand. 23* (1969) 1745.
11. Pihlaja, K., Pasanen, P. and Nurmi, T. *Unpublished results.*
12. Eliel, E., Rao, V. S. and Riddell, F. G. *J. Am. Chem. Soc. 98* (1976) 3583.
13. a. Beierbeck, H. and Saunders, J. K. *Can. J. Chem. 54* (1976) 2985; b. Lambert, J. B. and Vagenas, A. R. *Org. Magn. Reson. 17* (1981) 265 and 270.

Received September 9, 1982.