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A DIPOLE MOMENT STUDY OF THE STRUCTURES OF SOME KETENE ACETALS

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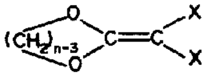
Abstract—The dipole moments of several acyclic and cyclic ketene acetals have been determined in benzene solution at 293 K using the Halverstadt-Kumler method. For ketene dialkyl acetals (alkyl = Me, Et) the results point to a predominance of the s-*cis*,s-*trans* rotamer, which disagrees with the conclusions drawn previously from ^{13}C NMR chemical shift data, i.e. the s-*cis*,s-*cis* form is the more stable species. In the case of 2-methoxyfuran, the dipole moment measurements confirm the previous findings based on the ^{13}C NMR spectra, *viz* the s-*cis* form is the predominating rotamer. The dipole moments and structures of some other ketene acetals are also discussed.

The spatial structures of some acyclic and cyclic ketene acetals were the subject of a recent ^{13}C NMR study.[1] In the present work, structural investigations on the following ketene acetals (1–3) are continued using the dipole moment approach:


1

No.	X	Y	R^1	R^2
1a	H	H	Me	Me
b	H	H	Et	Et
c	H	H	i-Pr	i-Pr
d	H	H	Et	$CH_2{=}CH$
e	H	H	$CH_2{=}C(Me)$	$CH_2{=}C(Me)$
f	Me	H	Et	Et
g	Cl	H	Et	Et
h	Cl	Cl	Me	Me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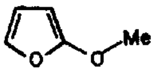
No.	X	n(=ring size)
2a	H	7
b	H	8
c	Cl	5
d	Cl	7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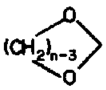
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a: n = 7
b: n = 8

For the sake of comparison, the dipole moments of the cyclic acetals **4a** and **4b** were also determined.

RESULTS AND DISCUSSION

The dipole moment of 2-methylene-1,3-dioxolane (**2**: n = 5) may be considered to arise from that of 1,3-dioxolane and the two mesomeric moments μ_m due to p-π conjugation in the $\mathrm{C{=}C}\genfrac{}{}{0pt}{}{\diagup\mathrm{O}}{\diagdown\mathrm{O}}$ system. The magnitude of μ_m is assumed to be 0.41 D (as in methyl vinyl ether[2]), directed at an angle of 26° to the axis of the C=C bond,[2] i.e. approximately from the O atom towards the β carbon of the vinyl group. From the μ value of 1,3-dioxolane ($\mu = 1.49\,D^2$), the dipole moment of 2-methylene-1,3-dioxolane is thus obtained as $\mu = 1.49 + 2 \cdot 0.41 \cos 26° = 2.23\,D$. Experimental μ data are not available for this compound because of its extremely ready polymerization, but the μ values of the corresponding 7- and 8-membered heterocycles **2a** and **2b** (Table 1) are in good agreement with this estimate. That these compounds and 2-methylene-1,3 dioxolane should have similar μ values

Table 1. The values of α, β, $P_{2\infty}$, R_D^{20} and μ for the compounds studied in this work

Compound	α	β	$P_{2\infty}/cm^3$	R_D^{20}/cm^3	μ/D
1a	2.14	−0.045	63.8	23.7	1.37
b	1.98	−0.026	81.5	33.0	1.50
c	2.20	−0.028	106.8	42.3	1.74
d	3.44	−0.228	104.1	32.5	1.84
e	1.63	0.006	90.2	41.3	1.50
f	1.19	0.015	73.5	37.6	1.28
g	4.50	−0.148	170.0	37.8	2.51
h	6.83	−0.365	235.4	33.3	3.11
2a	4.92	−0.093	139.7	30.9	2.28
b	4.50	−0.194	143.6	35.6	2.26
c	12.8	−0.602	392.8	31.1	4.17
d	11.1	−0.444	417.0	40.6	4.25
3	2.97	−0.226	81.1	25.6	1.62
4a	2.74	−0.163	81.8	26.7	1.61
b	1.47	−0.091	68.1	31.4	1.30

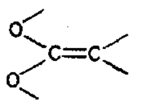
Table 2. A summary of the estimated μ values for some ketene acetals in their various configurations

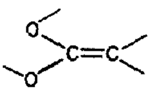
Compound	μ/D
1a	2.03 (s-cis,s-cis), 1.28 (s-cis,s-trans)
1b	2.20 (s-cis,s-cis), 1.26 (s-cis,s-trans)
1d	2.2 (s-cis,s-cis), 0.9 (s-cis,s-trans)
1f	1.20 (s-cis,s-trans)
1h	0.0 (s-cis,s-cis), 4.2 (s-trans,s-trans)
3	1.73 (s-cis), 0.90 (s-trans)

is supported by the good agreement between the dipole moments of the 5- and 7-membered chlorine containing compounds **2c** and **2d** (the μ values are 4.17 and 4.25 D, respectively). Interestingly, **2a** and **2b** have equal dipole moments, although those of the corresponding unsubstituted rings **4a** and **4b** differ by *ca* 0.3 D.

The μ values of **2a** and **2d** differ by 2.0 D, whereas those of ethylene and 1,1-dichloroethylene differ by 1.2–1.3 D.[3] Apparently the longer conjugated system in the ketene acetal **2a** is more readily polarizable by the inductive effect of the two Cl atoms than the simple C=C system of ethylene.

In the acyclic ketene acetals, rotation about the O–C(sp^2) bonds gives rise to rotational isomers some of which (*s-cis,s-cis*; *s-cis,s-trans*; *s-trans,s-trans*) are planar and the others (*s-cis,gauche*; *s-trans,gauche*; *gauche,gauche*) nonplanar. Considering the most stable structure of **1a**, all *gauche* forms appear unlikely on account of weak p-π conjugation in these structures.[1] The planar *s-trans,s-trans* form should have a μ value of *ca* 2.2 D, i.e. the same as that of **2a**, but this structure may be rejected as the most stable rotamer because of steric crowding between the Me groups. From the reported μ value of the *s-cis* form of methyl vinyl ether (1.05 D in benzene solution[4]) and the value of the angle between μ and the axis of the C=C bond (*ca* 15°, Ref. 5), the *s-cis,s-cis* form of **1a** is calculated (Scheme 1) to have a μ value of 2.03 D (CNDO/2 calculations[6] suggest $\mu = 2.49$ D). Similarly, for the *s-cis,s-trans* form of **1a** one obtains $\mu = 1.28$ D (the angle COC is assumed to be 121° as in methyl vinyl ether;[7] the vector 1.35 D represents the dipole moment of Me$_2$O in benzene solution[8] and the vector 0.41 D the mesomeric moment μ_m of methyl vinyl ether[2]). For the corresponding rotamers of **1b** the μ values are calculated to be 2.20 and 1.26 D, respectively, using the experimental dipole moments of ethyl vinyl ether ($\mu = 1.14$ D[9]) and diethyl ether ($\mu = 1.29$ D[8]). The reliability of these estimated μ values may be tested by comparison with experimental μ data for compound **1f**, which is known[1] to have a slightly nonplanar *s-cis,gauche* structure, not far from the planar *s-cis,s-trans* configuration. For the latter structure of **1f** one obtains $\mu = 1.20$ D by applying a correction due to the inductive effect[10] of the β Me group to the calculated μ value (1.26 D, see above) of the *s-cis,s-trans* rotamer of **1b**; the experimental dipole moment (1.28 D) is in fair agreement with the estimated one. Thus it is seen that the experimental μ values of **1a** and **1b** (1.37 and 1.50 D, respectively) clearly point to a predominance of the *s-cis,s-trans* rotamer in these compounds. This result, however, contradicts the conclusion drawn previously[1] from the ^{13}C NMR chemical shifts, i.e. the *s-cis,s-cis* rotamer is the most favored species. The previous results were based on the value of the chemical shift difference between the β olefinic carbons in **1b** and **1f**: if both compounds assume the same conformation (which cannot be *s-cis,s-cis* for **1f** on steric grounds), the shift difference for C-β should correspond to that (*ca* 11 ppm[1]) expected for a pure α effect of the Me group of **1f** alone. Since the experimental shift difference was *ca* 10 ppm higher than this figure, it was concluded that on going from **1b** to **1f**, a change in conformation occurs. The most probable conformational change appeared to be *s-cis,s-cis* → *s-cis,gauche* (slightly nonplanar).


s-cis,s-cis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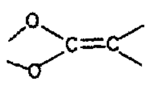
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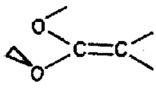
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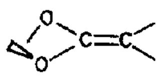
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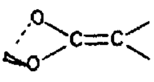

gauche,gauche

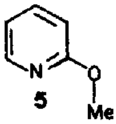
1a: *s-cis,s-cis* **1a**: *s-cis,s-trans*

Scheme 1

Since the ^{13}C NMR spectra were recorded in CDCl$_3$ solution while the dipole moment determinations were carried out in benzene, it might be thought that the contradictory results obtained from these experiments arise from solvent effects: the less polar *s-cis,s-trans* (or *s-cis,gauche*) rotamer is favored in the nonpolar solvent benzene. Accordingly, if **1b** and **1f** assume similar structures in a nonpolar solvent, the C-β shift of **1b** should increase significantly on going from CDCl$_3$ to benzene as solvent. However, a ^{13}C NMR spectrum of **1b** recorded in hexadeuterobenzene revealed a downfield drift of only 0.9 ppm for this carbon. Thus the solvents mentioned do not have a marked effect on the prevailing rotamer.

The problem encountered is settled if **1b** is taken to have the *s-cis,s-trans* structure in CDCl$_3$, but in that case it appears difficult to explain why the molecular structure changes to *s-cis,gauche* on introduction of a Me group at the β carbon (i.e. in **1b** → **1f**). The following reasoning is proposed. The planarity of the system in **1b** is favored by a good p-π overlap, which leads to an increase of negative charge density about C-β, and disfavored by a nonbonded repulsion between an Et group and the O atom of the second (*s-cis*) EtO group.[1] When one of the β hydrogens is replaced with a Me group, the electron repelling inductive effect of the Me group opposes the accumulation of negative charge about C-β, i.e. p-π conjugation, whereby the destabilizing nonbonded repulsion is strong enough to force the initially planar *s-trans* EtO group to assume a *gauche* structure. The nonplanar structure then leads to the considerably enhanced chemical shift value for the β carbon.

By vector addition of the dipole moments of furan (0.68 D,[3] direction from the ring towards the O atom) and methyl vinyl ether (1.05 D[4]), the s-*cis* and s-*trans* forms of 2-methoxyfuran (**3**) are calculated to have μ values of *ca* 1.73 and 0.90 D, respectively. The experimental μ value (1.62 D) supports the s-*cis* structure, in agreement with the ^{13}C NMR results.[1] For comparison, it is of interest to note that 2-methoxypyridine (**5**) is known[11] to prefer the s-*trans* structure. The favor of the s-*cis* structure in **3**, as compared to the favor of the s-*trans* structure in **5** or of the s-*cis*,s-*trans* structure in the acyclic ketene acetals **1a** and **1b**, probably follows from a difference in the magnitude of the electrostatic repulsion between the lone electron pairs of the heteroatoms in the s-*cis* (s-*cis*,s-*cis*) rotamer: in the acyclic and 6-membered heterocyclic compounds the lone electron pairs are closer to each other and hence their mutual repulsion is stronger than in **3** where the ring geometry allows a wider separation of the electron pairs and hence a smaller force of repulsion.



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The μ values calculated for the planar s-*cis*,s-*cis* and s-*cis*,s-*trans* (s-*trans* with respect of the EtO group) structures of **1d** are 2.2 and 0.9 D, respectively, suggesting a slight predominance of the former form (μ_{exp} = 1.84 D), as proposed previously.[12] Compound **1e** is definitely nonplanar[12] and the relatively low μ value (1.50 D) seems reasonable for a *gauche,gauche* form in which the moments of the ethereal linkages partially cancel each other.

Any of the planar structures seems improbable also for **1h** because of the presence of the two bulky Cl atoms at C-β. For a hypothetical planar s-*trans*,s-*trans* form μ should be approximately equal to the dipole moments of **2c** and **2d** (i.e. 4.2 D) and for a planar s-*cis*,s-*cis* rotamer one might expect a μ value of *ca* 0.0 D, since the combined moments of the two Cl atoms (2.0 D, see above) cancel the moment (2.03 D) calculated above for the s-*cis*,s-*cis* rotamer of **1a**. The experimental μ value (3.11 D) points to a *gauche,gauche* structure, closer to the s-*trans*,s-*trans* than to the s-*cis*,s-*cis* form.

EXPERIMENTAL

Materials. For **1**–**3** see Ref. 1. Compounds **4a** and **4b** were prepared from paraformaldehyde and the appropriate diols (1,4-butanediol and 1,5-pentanediol, respectively) by conventional methods. **4a**, b.p. 391 K at 101.3 kPa; **4b**, b.p. 402–403 K at 101.3 kPa.

Dipole moment determinations. See Ref. 10.

^{13}C NMR measurements. The ^{13}C NMR spectrum of **1b** was recorded at 15.03 MHz in C_6D_6 soln (20%, v/v) with TMS as internal reference. Shift values (ppm): 56.66 (C-β), 165.66 (C-α), 14.53 (CH_3), 63.46 (CH_2).

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