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# Nuclear Magnetic Resonance, Force Field, and MNDO Studies on 1-Methoxycycloalkenes

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**Abstract:** The <sup>1</sup>H, <sup>13</sup>C, and <sup>17</sup>O NMR spectra of 4- to 9-membered 1-methoxycycloalkenes have been recorded in CDCl<sub>3</sub> solution. The <sup>17</sup>O NMR chemical shifts reveal unexpectedly large and irregular variations with ring size. The other NMR shift data suggest that these variations are due to differences in the relative amounts of planar and nonplanar conformers about the  $O-C(sp^3)$  bond. The same NMR data also suggest that whereas the MeO groups of the 5- to 9-membered ethers adopt mainly the expected planar s-cis conformation, the 4-membered ether exists predominantly in the exceptional s-trans conformation. The geometries of and charge densities in these ethers have been studied by force field (COSMIC, MM2) and MNDO calculations.

Originally, the aim of the present study was to obtain <sup>17</sup>O NMR shift data for the title compounds, a special class of  $\alpha,\beta$ -unsaturated (vinyl) ethers. Since the O atom is exocyclic to the cycloalkene ring, and therefore relatively remote from the changing chemical environment with varying ring size, the effect of ring size on  $\delta(^{17}\text{O})$  was expected to be small, and possibly regular. The experimental data, however, were not in line with this assumption: the shift values varied irregularly and the range was unexpectedly large, 14 ppm:



To clarify the factors responsible for the observed shift values, the information provided by <sup>1</sup>H and <sup>13</sup>C NMR spectral data was scrutinized, in combination with force field (MM2, COSMIC) and MNDO calculations.

#### EXPERIMENTAL

The title ethers were prepared from the appropriate cyclic ketones,  $HC(OMe)_3$ , and MeOH with *p*-TsOH as catalyst,<sup>1</sup> with or without isolation of the intermediate dimethoxy acetals. Boiling points (°C/torr): **1** 75-76/760; **2** 109-110/756 (lit.<sup>2</sup> 112.5-113.5); **3** 141-142/765 (lit<sup>2</sup>. 137-138), **4** 55-56/18 (lit.<sup>2</sup> 91-92/87), **5** 39-40/3 (lit.<sup>2</sup> 70.5-71.5/13); **6** 79-80/9.

The <sup>1</sup>H, <sup>13</sup>C, and <sup>17</sup>O NMR spectra were recorded in CDCl<sub>3</sub> solution at 21 °C on a Jeol GX-400 NMR spectrometer operating at frequencies of 399.8, 100.5, and 54.2 MHz, respectively. A solvent:solute volume ratio of 2:1 was used for recording the <sup>17</sup>O NMR spectra, with 1,4-dioxane (10 vol-%) as internal standard. The instrumental parameters were as follows: 20  $\mu$ s pulse width, 75 ms pulse delay, 8k data points, 50 ms acquisition time, and 75 ms repetition time. The internal standard was assigned a shift value of -1.3 ppm relative to that of H<sub>2</sub>O (*i.e.* the dioxane signal was found 1.3 ppm upfield from that of water); this value was obtained as a mean of a large number of repeated measurements of 1,4-dioxane in CDCl<sub>3</sub>. The <sup>17</sup>O NMR shift values reported in this work are thus on the water scale, and are probably accurate within 1-2 ppm. The half-height widths (in Hz) were: 150 (1), 240 (2), 330 (3), 340 (4), 410 (5), and 410 (6).

#### **RESULTS AND DISCUSSION**

Obviously, the irregularities in the <sup>17</sup>O NMR chemical shifts of **1-6** are not explainable by variations in the inductive and shielding effects of the different ring sizes; some other factor(s) must be involved. The present compounds, being  $\alpha,\beta$ -unsaturated olefinic ethers, are characterized by a possibility of p- $\pi$  conjugation in the vinyloxy system:

$$-0-C=C \leftrightarrow -\dot{O}=C-\bar{C}$$

From our point of view, this phenomenon has two important consequencies. First, the positive charge on the O atom causes the <sup>17</sup>O NMR signal of vinyl ethers to appear several tens of ppm downfield from that of related saturated ethers;<sup>3</sup> moreover, the value of the chemical shift depends essentially on the efficiency of this conjugative interaction. As an example from the field of aromatic ethers, the <sup>17</sup>O NMR signal of 2,6-dimethylanisole, in which p- $\pi$  conjugation is markedly hindered by the two *ortho* Me groups, is found some 30 ppm upfield from that of the unsubstituted anisole.<sup>4</sup> Second, the partial double bond character of the O-C(*sp*<sup>2</sup>) bond leads to rotational isomerism about this bond (Scheme I). Planar structures are favorable for p- $\pi$  interaction; in fact, the planar s-*cis* conformer has been found to be the most stable form of methyl vinyl ether, in addition to a less stable form whose structure (a planar s-*trans* or a nonplanar gauche form) has been subject to considerable controversy (for recent work, and pertinent references therein, see Ref. 5).

Accordingly, the variations in the <sup>17</sup>O NMR chemical shifts of **1-6** may be indicative of varying strengths of  $p-\pi$  conjugation in these compounds. If this is the case, the highest contributions of  $p-\pi$  interaction are found in the 4- and 7-membered ring sizes. However, since there is



no apparent reason for why any of the MeO groups of the present compounds could not assume the same planar s-cis conformation, one has to conclude that, in addition to the s-cis (and possibly the planar s-trans) conformers, varying amounts of nonplanar conformers exist in the present compounds (the nonplanar forms are statistically favored over the planar forms). Accordingly, the highest contribution of nonplanar conformers is found in 2, the lowest in 1. Unfortunately, the validity of this interpretation cannot be tested by comparison with experimental structural data, which are available only for the 6-membered ether (3): electron diffraction measurements show that in the gas phase 3 consists mainly, if not entirely, of the (expected) planar s-cis form.<sup>6</sup> Hence, in the absence of structural data for the other compounds, one must turn to the information provided by the other NMR spectroscopic data, as well as to that afforded by computational methods.

### <sup>1</sup>H NMR spectra

The proton spectra of 1-6 are given in Table 1. For comparison, the Table also contains related data for the corresponding cycloalkenes<sup>7</sup> and 1-trimethylsilyloxycycloalkenes.<sup>8</sup> Due to  $p-\pi$  conjugation in  $\alpha,\beta$ -unsaturated ethers, electron density on C- $\beta$  of the vinyl group is increased, which leads to a typical upfield shift of ca. 1 ppm, relative to the corresponding alkene, for the signal of the proton bound to this carbon.<sup>9</sup> In the present compounds, the magnitude of the upfield shift depends noticeably on ring size: it is remarkably high, 1.44 ppm, for 1 but only 0.98 ppm for 3. For comparison, in the open chain analog of the present ethers, (*E*)-2-methoxy-2-butene (7), the olefinic proton (at  $\delta$  4.20<sup>10</sup>) absorbs 1.25 ppm upfield from that



(at  $\delta$  5.45<sup>11</sup>) of the respective olefin, (Z)-2-butene (8). Thus the exceptionally large upfield shift of the olefinic proton of 1 supports the view of enhanced p- $\pi$  conjugation, and of high contribution of planar conformers, in this ether.

The <sup>1</sup>H NMR chemical shifts of the methylene group protons in the -CH<sub>2</sub>-C=C moieties give additional information. In the reference compound 7, the protons of the Me group bound to C- $\beta$  of the vinyl group absorb at  $\delta$  1.53,<sup>10</sup> close to the shift value ( $\delta$  1.60<sup>11</sup>) of the Me groups of the respective olefin 8, and 0.15 ppm upfield from the signal of the Me group attached to C- $\alpha$ .

Ring size	R	С=С-Н	MeO	Other
4	MeO	4.51	3.58	2.05 (m, 3.2 Hz, 2H), 2.59 (m, 3.2 Hz, 2H)
	TMSO	4.52		
	н	5. <del>9</del> 5		2.57
5	MeO	4.45	3.60	2.2-2.3 (m, 4H), 1.88 (m, 7.6 Hz, 2H)
	TMSO	<b>4.49</b>		
	н	5.60		2.28 (4H), 1.90 (2H)
6	MeO	4.61	3.50	2.0-2.1 (m, 4H), 1.67 (m, 2H), 1.54 (m, 2H)
	TMSO	4.71		
	н	5.5 <del>9</del>		1.96 (4H), 1.65 (4H)
7	MeO	4.70	3.43	2.25 (m, 2H), 2.03 (m, 2H), 1.4-1.8 (m, 6H)
	TMSO	4.93		
	H	5.71		2.11
8	MeO	4.47	3.48	2.24 (m, 2H), 2.08 (m, 2H), 1.55 (m, 2H), 1.48 (m, 6H)
	TMSO	4.67		
	н	5.56		2.11, 1.5
9	MeO	4.46	3.49	2.23 (m, 2H), 2.12 (m, 2H), 1.58 (m, 2H), 1.48 (m, 8H)
	TMSO	4.62		

**Table 1.** <sup>1</sup>H NMR Chemical Shift Data for 1-Methoxycycloalkenes (R = MeO), 1-Trimethylsilyloxycycloalkenes (R = TMSO),<sup>8</sup> and Cycloalkenes (R = H).<sup>7</sup>

Differences in the chemical shifts of the olefinic proton between R = H and R = MeO, as well as between R = TMSO and R = MeO:

	Ring size									
	4	5	6	7	8	9				
$\delta(\mathbf{R} = \mathbf{H}) - \delta(\mathbf{R} = \mathbf{MeO})$	1.44	1.15	0.98	1.01	1.09					
$\delta(R = TMSO) - \delta(R = MeO)$	0.01	0.04	0.10	0.23	0.20	0.16				

In the ethers 2-6, the differences between the <sup>1</sup>H NMR chemical shifts of the two methylene groups bound to the C=C system are similarly 0.1-0.2 ppm. However, in 1 the site of absorption of one of the methylene groups coincides with that of cyclobutene whereas the protons of the other methylene group are shielded relatively by as much as ca. 0.5 ppm. The obvious conclusion is that in 1 it is the methylene group bonded to C- $\alpha$  (C-1) which is the more shielded one, contrary to the situation in 7, and probably in 2-6 as well. (A distinction between the two methylene groups of 1 could not be made from the value of the coupling constant with the olefinic proton, since this coupling is negligible). The marked increase in shielding experienced by the protons of the C-4 methylene group of 1 thus suggest a drastic change towards dominance of the *s*-trans form in the rotameric mixture. In Table 1, the chemical shifts of the olefinic protons of 1-6 are also compared with those of the corresponding 1-trimethylsilyloxyethers. This group of ethers is structurally related to the present compounds, but due to the bulkiness of the trimethylsilyl group, planar rotameric forms of the silyl ethers are crowded, and hence the nonplanar gauche forms are likely to dominate in all ring sizes, with the possible exception of the 4-membered ring. Table 1 shows that the difference in chemical shifts for the methyl and trimethylsilyl ethers is negligible for the 4-membered ethers, then increases up to the 7-membered ring size, after which it begins to diminish again. This suggests that the 4-membered methyl and trimethylsilyl ethers may have similar spatial structures whereas the difference in structure is most pronounced for the 7-membered ethers.

### <sup>13</sup>C NMR spectra

The <sup>13</sup>C NMR chemical shifts of the title compounds, together with those for the corresponding olefins and silyl ethers, are shown in Table 2. While distinction between the olefinic carbons is easy, with C-1 always resonating downfield from C-2, signal assignment for the other ring atoms of 1-6 is a less simple task. As to 2 and 3, the assignments are based on comparison of the spectra with those for several Me-substituted derivatives,<sup>12</sup> and may be considered reliable. In these ethers, the main problem is to differentiate between the two C atoms bound to the olefinic system. The assignments achieved show that the carbon bound to C-1 has a higher shift value (by 2.8 and 4.3 ppm for 2 and 3, respectively) than the carbon bound to C-2, in line with the fact that the corresponding difference is 4.0 ppm in 7.13 This finding was utilized in signal assignment for 4-6, but it did not seem to work for 1: here one of the C atoms bound to the C=C system absorbed very close to the corresponding signal of cyclobutene while the other resonated ca. 12 ppm upfield. Since it was difficult to see any reason for why C-3 of 1 could experience a shielding effect of 12 ppm relative to the corresponding carbon of cyclobutene, it seemed reasonable to assign the latter signal to C-4 and the former to C-3. This conclusion was confirmed by an off-resonance <sup>13</sup>C NMR spectrum of 1: the high field signal ( $\delta$  19.6) appeared as a well-defined triplett (with a coupling constant of 140 Hz) with no additional coupling to more remote protons visible whereas the lines of the corresponding triplet at  $\delta$  31.1 (J 140 Hz) were clearly broader and less well-defined, bearing evidence to coupling with an additional vicinal proton (the olefinic proton). For comparison, in 7 the shift of the C-4 atom (the carbon bound to C- $\beta$ ), 11.9 ppm, is close to the corresponding signal of 8 (11.4 ppm<sup>14</sup>) while the C-1 atom of 7 (at & 15.8 ppm) absorbs 4.4 ppm downfield from that of 8. Accordingly, both the <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts of 1 show that the atoms of the methylene group linked to C-1 are strongly shielded, relative to those of cyclobutene.

The <sup>13</sup>C NMR chemical shifts of 1-6 are compared with those of the respective olefins and silyl ethers in Table 3. As to the olefinic carbon C-2, the MeO group induced shielding effect is highest (42.2 ppm) for 1, pointing to enhanced conjugation and high contribution of planar conformers in this compound. The marked shielding effect, 11.8 ppm, of the MeO group on C-4 of 1 is truly exceptional in the series: in 2 the same effect (on C-5) is negligible, and becomes

n	R	C-1	C-2	C-8	C-4	C-5	C-6	C-7	C-8	C-9	MeO
4	MeO	153.400	95.000	31.100	19.600						55.200
	TMSO	148.500	102.200	<b>34.40</b> 0	20.000						
	н	137.200	137.200	<b>31.400</b>	31.300						
5	MeO	161.100	93.300	29.000	21.500	31.800					56.700
	TMSO	155.300	101.400	29.100	21.600	33.900					
	н	130.800	130.800	32.800	23.300	32.800					
6	MeO	155.400	93.100	23.500	22.800	22.900	27.800				53.800
	TMSO	150.600	103.300	24.200	23.500	22.800	30.300				
	н	127.400	127.400	25.400	23.000	23.000	25.400				
7	MeO	162.000	96.000	28.200	25.300	32.200	25.600	33.700			53.900
	TMSO	156.400	107.500	28.300	25.600	31.900	25.600	35.900			
	н	132.700	132.700	29.600	28.000	32.700	28.000	29.600			
8	MeO	158.300	94.000	25.000	26.200	28.300	29.500	26.300	31.100		53.600
	TMSO	153.200	104.600	25.700	26.600	28.100	31.300	25.900	31.400		
	н	130.400	130.400	26.000	27.000	29.800	29.800	27.000	26.000		
9	MeO	158.100	96.100	24.700	24.900	25.400	28.000	26.100	25.300	29.400	53.800
	TMSO	152.800	106.500	25,400	25.800	25.800	27.800	25.800	24,700	30,700	

**Table 2.** <sup>18</sup>C NMR Chemical Shift Data for 4- to 9-Membered Cycloalkenes (R = H),1-Methoxycyclocycloalkenes (R = MeO), and 1-Trimethylsilyloxycycloalkenes (R = TMSO).

Table 3.	8. Differential <sup>13</sup> C NMR Chemical Shifts of 1-Methoxyalkenes Relative to 1-	Trimethyl-
silyloxycy	cycloalkenes and to Cycloalkenes.	

n	R	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9
4	TMSO	4.900	-7.200	-3.300	-0.400					
	н	16.200	-42.200	-0.300	-11.800					
5	TMSO	5.800	-8.100	-0.100	-0.100	-2.100				
	н	30.300	-37.500	-3.800	-1.800	-1.000				
6	TMSO	4.800	-10.200	-0.700	-0.700	0.100	-2.500			
	н	28.000	-34.300	-1.900	-0.200	-0.100	2.400			
7	TMSO	5.600	-11.500	-0.100	-0.300	0.300	0.000	-2.200		
	н	29.300	-36.700	-1,400	-2.700	-0.500	-2.400	4.100		
8	TMSO	5.100	-10.600	-0.700	-0.400	0.200	-1.800	0.400	-0.300	
	н	27.900	-36.400	-1.000	-0.800	-1.500	-0.300	-0.700	5.100	
9	TMSO	5.300	-10.400	-0.700	-0.900	-0.400	0.200	0.300	0.600	-1.300

deshielding in the larger ring sizes. The deshielding effect, 16.2 ppm, of the MeO group of 1 on the chemical shift of C-1 is also exceptional.

In comparison with the <sup>13</sup>C NMR chemical shifts of the silyl ethers, the data of Table 3 for the C-2 atoms of **1-6** point to enhanced p- $\pi$  conjugation in the MeO derivatives. The difference in the strength of conjugation is highest for the 7-membered ethers [ $\Delta\delta(C-2) = 11.5$  ppm], and lowest for the 4-membered ethers [ $\Delta\delta(C-2) = 7.2$  ppm]. This is reasonable since the two types of ethers can most easily approach the same rotameric composition, and chances for conjugation, in the 4-membered ring size, rather than in the large-ring compounds where the planar *s*-cis structure, readily adopted by the methyl ethers, is unfavorable for the bulky trimethylsilyl ethers.

## Charge calculations by the MNDO method

For additional information on the present compound, the net atomic charges were calculated by the MNDO method<sup>16</sup> for the s-cis form of the methyl ethers **1-6**, as well as for the corresponding cycloalkenes (Table 4). From these values the effects of the MeO substituent on charge density on the various ring atoms were obtained by subtraction, and the results are also reported in Table 4. A marked polarization of the C=C bond by the MeO substituent is shown by the differential charge densities on C-1 and C-2, and the data suggest that this phenomenon is likely to increase slightly with increasing ring size (at least up to the 7-membered ring size). For comparison, similar calculations on the acyclic compound **7** gave the net atomic charges of 0.095 and -0.211, respectively, on the  $\alpha$  and  $\beta$  carbons of the C=C bond, and a net atomic charge of -0.101 on each of the olefic carbons of **8**. Thus the polarization due to the MeO substituent of **7** amounts to 0.196 and -0.110 units of charge on C- $\alpha$  and C- $\beta$ , respectively, an effect comparable in magnitude to those found in the 7- to 9-membered methyl ethers.

The phenomenon of p- $\pi$  conjugation in vinyl ethers leads to a shift of negative charge from the O atom towards C- $\beta$  of the C=C bond, which leaves the O atom positively charged, relative to the O atom of an unconjugating ether. This effect is reproduced by the MNDO calculations: when the net atomic charges on the O atoms of 1-6 are compared with those calculated for the respective saturated ethers (methoxycyclobutane, -pentane, etc.), the net atomic charges on the O atoms of the latter ethers are found to be consistently more negative than those for 1-6, viz., -0.330, -0.334, -0.348, -0.352, -0.353, and -0.353 units of charge for the 4- to 9-membered methyl cycloalkyl ethers. By subtraction one finds that in 1-6, the net positive charges on the oxygen atoms are 0.080, 0.063, 0.091, 0.058, 0.058, and 0.056 units of charge, respectively. For comparison, the net atomic charges on the O atoms of 7 and the corresponding saturated ether, 2-methoxybutane, are calculated to be -0.300 and -0.349, respectively, pointing to a transfer of 0.049 units of charge from the O atom of 7, which is close in magnitude to the effects found in the 7- to 9-membered vinyl ethers. Accordingly, the atomic charges on the O atoms of 1-6 suggest p- $\pi$  conjugation to be more effective in the smaller ring sizes while inspection of the magnitude of polarization of the C=C bond gave a different result. Thus, on average, the obvious message of the MNDO calculations is that the strength of p- $\pi$  conjugation is essentially independent of ring size in the s-cis conformers of the ethers 1-6. This confirms the view proposed

R	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	0
н	-0.117	-0.117	-0.007	-0.007						
MeO	0.048	-0.212	0.013	0.020						-0.250
H	-0.106	-0.106	0.013	-0.022	0.013					
MeO	0.075	-0.209	0.035	-0.026	0.033					-0.271
н	-0.096	-0.0 <del>96</del>	0.025	-0.011	-0.011	0.025				
MeO	0.080	-0.194	0.046	-0.016	-0.018	0.037				-0.257
н	-0.092	-0.092	0.029	-0.008	-0.007	-0.008	0.029			
MeO	0.102	-0.204	0.050	-0.011	-0.009	-0.009	0.040			-0. <b>29</b> 4
н	-0.092	-0.091	0.031	-0.004	-0.005	-0.005	-0.003	0.031		
MeO	0.103	-0.202	0.052	-0.007	-0.006	-0.006	-0.005	0.043		-0.295
н	-0.090	-0.090	0.032	-0.003	-0.004	-0.004	-0.003	-0.004	0.032	
MeO	0.105	-0.201	0.055	-0.005	-0.006	-0.004	-0.006	-0.003	0.044	-0.297
	R H MeO H MeO H MeO H MeO H MeO	R         C-1           H         -0.117           MeO         0.048           H         -0.106           MeO         0.075           H         -0.096           MeO         0.080           H         -0.092           MeO         0.102           H         -0.092           MeO         0.103           H         -0.092           MeO         0.103           H         -0.092           MeO         0.103           H         -0.090	R         C-1         C-2           H         -0.117         -0.117           MeO         0.048         -0.212           H         -0.106         -0.106           MeO         0.075         -0.209           MeO         0.075         -0.209           H         -0.096         -0.096           MeO         0.080         -0.194           H         -0.092         -0.092           MeO         0.102         -0.204           H         -0.092         -0.091           MeO         0.103         -0.202           H         -0.092         -0.091           MeO         0.103         -0.202           H         -0.092         -0.091           MeO         0.103         -0.202           MeO         0.103         -0.203           MeO         0.103         -0.204           H         -0.090         -0.090	R         C-1         C-2         C-3           H         -0.117         -0.007         -0.007           MeO         0.048         -0.212         0.013           H         -0.106         -0.106         0.013           MeO         0.075         -0.209         0.035           MeO         0.075         -0.096         0.025           MeO         0.080         -0.194         0.046           H         -0.092         -0.092         0.029           MeO         0.102         -0.204         0.050           H         -0.092         -0.091         0.031           MeO         0.102         -0.204         0.051           H         -0.092         -0.091         0.031           MeO         0.103         -0.202         0.052           H         -0.090         -0.091         0.031           MeO         0.103         -0.204         0.032           H         -0.090         -0.090         0.032           H         -0.090         -0.090         0.032	R         C-1         C-2         C-3         C-4           H         -0.117         -0.007         -0.007           MeO         0.048         -0.212         0.013         0.020           H         -0.106         -0.106         0.013         -0.022           MeO         0.075         -0.209         0.035         -0.026           MeO         0.075         -0.209         0.035         -0.026           H         -0.096         -0.096         0.025         -0.011           MeO         0.080         -0.194         0.046         -0.016           H         -0.092         -0.092         0.029         -0.008           MeO         0.102         -0.204         0.050         -0.011           H         -0.092         -0.091         0.031         -0.004           MeO         0.103         -0.202         0.052         -0.007           H         -0.090         -0.090         0.032         -0.003           MeO         0.103         -0.204         0.052         -0.003           H         -0.090         -0.090         0.032         -0.003           MeO         0.105         -0.201	R         C-1         C-2         C-3         C-4         C-5           H         -0.117         -0.007         -0.007         -           MeO         0.048         -0.212         0.013         0.020         -           H         -0.106         -0.106         0.013         -0.022         0.013           MeO         0.075         -0.209         0.035         -0.026         0.033           MeO         0.076         -0.096         0.025         -0.011         -0.011           MeO         0.080         -0.194         0.046         -0.016         -0.013           MeO         0.080         -0.194         0.046         -0.016         -0.017           MeO         0.102         -0.092         0.029         -0.008         -0.007           H         -0.092         -0.091         0.031         -0.011         -0.005           H         -0.092         -0.091         0.031         -0.004         -0.005           H         -0.092         -0.091         0.032         -0.007         -0.004           HeO         0.103         -0.204         0.032         -0.003         -0.004           HeO         0.10	R         C-1         C-2         C-3         C-4         C-5         C-6           H         -0.117         -0.007         -0.007         -	R         C-1         C-2         C-3         C-4         C-5         C-6         C-7           H         -0.117         -0.017         -0.007         -0.007         -	RC-1C-2C-3C-4C-5C-6C-7C-8H $-0.117$ $-0.007$ $-0.007$ $-0.007$ $-0.007$ $-0.007$ $-0.007$ $-0.007$ MeO $0.048$ $-0.212$ $0.013$ $0.020$ $-0.013$ $-0.022$ $0.013$ $-0.016$ $-0.016$ MeO $0.075$ $-0.209$ $0.035$ $-0.026$ $0.033$ $-0.011$ $-0.025$ $-0.011$ $-0.016$ MeO $0.075$ $-0.209$ $0.035$ $-0.011$ $-0.011$ $0.025$ $-0.011$ $-0.012$ $-0.096$ $-0.096$ MeO $0.080$ $-0.194$ $0.046$ $-0.018$ $-0.007$ $-0.008$ $0.029$ $-0.011$ MeO $0.012$ $-0.092$ $0.029$ $-0.008$ $-0.007$ $-0.008$ $0.029$ $-0.011$ MeO $0.102$ $-0.091$ $0.031$ $-0.004$ $-0.005$ $-0.003$ $0.031$ MeO $0.103$ $-0.201$ $0.032$ $-0.007$ $-0.006$ $-0.003$ $0.031$ MeO $0.103$ $-0.202$ $0.052$ $-0.007$ $-0.005$ $-0.005$ $-0.003$ $0.031$ MeO $0.103$ $-0.202$ $0.052$ $-0.007$ $-0.006$ $-0.006$ $-0.003$ $-0.004$ MeO $0.103$ $-0.202$ $0.052$ $-0.003$ $-0.004$ $-0.004$ $-0.006$ $-0.004$ MeO $0.105$ $-0.201$ $0.055$ $-0.005$ $-0.006$ $-0.004$ $-0.006$ $-0.006$	RC-1C-2C-3C-4C-5C-6C-7C-8C-9H $-0.117$ $-0.008$ $-0.016$ $-0.016$ $-0.016$ $-0.016$ $-0.017$ $-0.008$ $-0.029$ $-0.008$ $-0.017$ $-0.008$ $-0.029$ $-0.008$ $-0.017$ $-0.008$ $-0.029$ $-0.008$ $-0.017$ $-0.008$ $-0.029$ $-0.029$ $-0.008$ $-0.007$ $-0.008$ $-0.029$ $-0.011$ $-0.008$ $-0.029$ $-0.011$ $-0.018$ $-0.029$ $-0.011$ $-0.008$ $-0.029$ $-0.011$ $-0.008$ $-0.029$ $-0.011$ $-0.008$ $-0.029$ $-0.011$ $-0.018$ $-0.029$ $-0.011$ $-0.008$ $-0.029$ $-0.011$ $-0.008$ $-0.029$ $-0.011$ $-0.008$ $-0.029$ $-0.011$ $-0.008$ $-0.003$ $-0.011$ $-0.008$ $-0.003$ $-0.011$ $-0.008$ $-0.003$ $-0.011$ $-0.008$ $-0.003$ $-0.011$ $-0.008$ $-0.003$ $-0.011$ $-0.008$ $-0.003$ $-0.011$ $-0.008$ $-0.003$ $-0.011$ $-0.008$ $-0.003$ $-0.011$ $-0.008$ $-0.003$ $-0.011$ $-0.008$ $-0.0$

 Table 4. Net Atomic Charges on Various Atoms of Cycloalkenes and 1-Methoxycycloalkenes

 by the MNDO Method.

Differences in the net atomic charges between 1-methoxycycloalkenes and cycloalkenes:

4	0.165	-0.095	0.020	0.027					
5	0.181	-0.103	0.022	-0.004	0.020				
6	0.176	-0.098	0.021	-0.005	-0.007	0.012			
7	0. <b>194</b>	-0.112	0.021	-0.003	-0.002	-0.001	0.011		
8	0.195	<b>-0.111</b>	0.021	-0.003	-0.001	-0.001	-0.002	0.012	
9	0.195	-0.111	0.023	-0.002	-0.002	0.000	-0.003	0.001	0.012

Total polarization of the olefinic system of 1-methoxycycloalkenes as judged by the differences in the net atomic charges between C-1 and C-2:

Ring size	4	5	6	7	8	9
Difference	0.260	0.284	0.274	0.306	0.306	0.306

earlier, *viz.*, the variations observed in the NMR chemical shifts of the various nuclei of the vinyloxy system do not arise from differences in the inherent strengths of conjugation in the s-*cis* conformers, but from differences in the planar/nonplanar conformer ratios.

The charges on the other ring atoms are also interesting, especially those on the two C atoms bonded to the C=C system. Considering the differences in charge on C-3 between 1-6

and the respective cycloalkenes, Table 4 shows that in the ethers the excess charges on this allylic carbon atom are remarkably constant, ca. 0.021 units of charge, in line with the difference, 0.022, in the atomic charges (0.090 and 0.068, respectively) between the corresponding carbons of 7 and 8. On the other hand, the excess charges on the C atom bound to C- $\alpha$  of the C=C bond decrease from 0.027 in 1 to ca. 0.012 in the large ring compounds. The latter figure agrees with the difference, 0.011 units of charge, calculated from the net atomic charges of 0.079 and 0.068 on the respective C atoms of 7 and 8. Once again, the features of the large ring compounds are repeated in the open chain analogs.

### Geometry calculations

Finally, the structures of 1-7 were optimized by the MM2,<sup>15</sup> COSMIC,<sup>16</sup> and MNDO<sup>15</sup> methods. As a starting geometry of the ring compounds, the most stable conformation of the parent cycloalkene was used (see Ref. 17 for cyclopentene to cyclooctene and Ref. 18 for cyclononene; for 1 the planar cyclobutene structure was used). For consistency, the MeO group was taken to assume the planar s-cis conformation in all ring sizes. The calculated values for some geometrical parameters of highest interest, together with their averages from the different approaches, and in combination with experimental data where available, are shown in Table 5. Generally, in the large ring ethers, the parameter values are close to those for the acyclic reference compound 7. With decreasing ring size, the C=C and O-C( $sp^2$ ) bonds become slightly shorter. Moreover, as the C-C=C bond angle decreases and the O-C=C bond angle widens in the same sequence, the value of the ethereal bond angle COC decreases by ca. 3°. As a consequence of these structural changes, the distance between the Me group and C-2 increases by ca. 0.1 Å.

The question of varying conformer compositions of 1-6 might be attempted to solve by estimation of the relative energies of the s-cis and non-s-cis conformers by force field calculations. In this respect the best candidate is the MM2 method which has been parameterized for processes involving rotation of the MeO group about the  $O-C(sp^2)$  bond.<sup>19</sup> In addition to its relative energy, the structure of the non-s-cis conformer is also of interest. The latter may be characterized by means of the value of the torsional angle about the O-C( $sp^3$ ) bond (0° for the s-cis, 180° for the s-trans form). The following relative energies, in kJ mol<sup>-1</sup>, and torsional angles were obtained for the non-s-cis conformer: 1 7.4 (147°), 2 6.6 (142°), 3 5.8 (137°), 4 8.2 (128°), 5 7.5 (127°), and 6 5.3 (138°). Thus the MM2 method predicts that in each case, even in the 4-membered ring size, the non-s-cis conformer is of higher energy (by 5-8 kJ mol<sup>-1</sup>) than the s-cis form. In addition, the torsional angle of the less stable conformer is calculated to be farthest from that of the s-trans form in the 7- and 8-membered rings, and to reach the highest value, 147°, in 1, still 33° away from the planar s-trans form. In the absence of additional experimental data, the results of the force field calculations might seem reasonable. However, they provide no explanation of the observed NMR shift data. Moreover, it should be stressed that parameterization of the MM2 force field for vinyl ethers is far from perfect, and serious errors in energy calculations (and probably in structure calculations, too) may occur. For example, the method predicts that in  $\alpha,\beta$ -dialkylsubstituted methyl vinyl ethers, the E isomer (like

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**Table 5.** Structural Data for Some 1-Methoxycycloalkenes by the MM2, COSMIC, and MNDOMethods. For Comparison, Related Data for (E)-2-MeO-2-butene are Also Included.

				Ring si	ze			2-MeO-
	Method	4	5	6	7	8	9	2-butene
∠(COC)	MM2	115.2	116.9	118.4	118.6	118.8	118.8	118.9
	COSMIC	118.5	119.8	120.8	120.9	<b>120.9</b>	120.9	121.0
	MNDO	120.6	122.4	121.7	124.5	125.5	124.9	125.1
	Mean	118.1	119.7	1 <b>20.3</b>	121.8	121.7	121.5	121.7
	Ехр.			119.7				
∠(0-C=C)	MM2	134.8	129.4	126.3	126.1	125.6	125.9	125.6
	COSMIC	1 <b>26.9</b>	124.1	122.5	121.0	122.1	121.8	122.4
	MNDO	1 <b>39.4</b>	131.1	128.3	124.8	126.1	124.4	124.2
	Mean	1 <b>33.</b> 7	128.2	125.7	1 <b>24.</b> 0	124.6	124.0	124.1
	Exp.			122.5				
$\angle$ (C-C <sub>1</sub> =C <sub>2</sub> )	MM2	94.7	110.5	120.1	119.9	121.1	121.5	123.0
	COSMIC	95.2	111.8	122.2	122.9	124.0	125.1	122.5
	MNDO	94.5	112.5	120.0	125.0	122.2	<b>126</b> .1	127.0
	Mean	94.8	111.6	120.8	1 <b>22.6</b>	122.4	124.2	1 <b>24.2</b>
	Exp.			124.2				
d(C=C)/Å	<b>MM2</b>	1.337	1.341	1.346	1.345	1.346	1.347	1.348
	COSMIC	1.329	1.340	1.349	1.348	1.350	1.350	1.348
	MNDO	1.364	1.362	1.360	1.360	1.360	1.363	1.363
	Mean	1.343	1.348	1.352	1.351	1.352	1.353	1.353
	Exp.			1.333				
d(O-C( <i>sp</i> *))/Å	MM2	1.355	1.364	1.372	1.372	1.374	1.373	1.374
	COSMIC	1.378	1.380	1.382	1.383	1.382	1.383	1.382
	MNDO	1.340	1.352	1.359	1.365	1.363	1.367	1.368
	Mean	1.358	1.365	1.371	1.373	1.373	1.374	1.375
	Ехр.			1.364				
$d(\underline{C}H_3-C_2)/\dot{A}$	MM2	2.920	2.867	2.850	2.849	2.844	2.851	2.849
	COSMIC	2.856	2.839	2.835	2.834	2.831	2.832	2.835
	MNDO	3.108	3.002	2.909	2.934	2.960	2.937	2.937
r	Mean	<b>2.96</b> 1	<b>2.903</b>	2.865	2.872	2.878	2.873	2.874

7) is less stable than its geometrical isomer, whereas the empirical data (thermodynamic,<sup>20</sup> <sup>13</sup>C NMR,<sup>13</sup> and <sup>17</sup>O NMR<sup>21</sup>) show conclusively that for small alkyl groups, the reverse is true. (To take an example, 7 is calculated to be 7.5 kJ mol<sup>-1</sup> less stable than its geometrical isomer, whereas the experimental enthalpy difference is 9.9 kJ mol<sup>-1</sup>, in favor of 7).

As stated above, the MM2 calculations fail to support the conclusion drawn from the proton and carbon spectra, *viz.*, the most stable conformer of 1 is the unexpected s-*trans* form. However, a simple inspection of molecular models gives support for this conclusion. Considering the distances of closest approach between the hydrogen atoms of the Me group and those of the methylene group bonded to C-1 of this conformer one arrives at the following figures: 1.2-1.3 Å in 4-7, 1.8 Å in 3, 2.0 Å in 2, and 2.6 Å in 1 (the marked differences in the estimated distances are due, besides to ring size, also to ring conformation). Accordingly, only in the 4-membered ether does the distance of closest approach exceed twice the van der Waals radius (2.4 Å) of a hydrogen atom.

## SUMMARY

In summary, the evidence given by the <sup>17</sup>O, <sup>13</sup>C, and <sup>1</sup>H NMR chemical shifts shows that extensive p- $\pi$  conjugation exists, and planar conformers dominate, in each of the present compounds. The highest contributions of planar forms are found in the 4- and 7-membered 1-methoxycycloalkenes; moreover, in the 5- to 9-membered ethers, the s-*cis* conformers expectedly prevail. However, both the <sup>13</sup>C and <sup>1</sup>H NMR data strongly point to an exceptional predominance of the planar s-*trans* conformer in 1-methoxycyclobutene (1). If this interpretation is correct, it appears that this compound is the only known derivative of methyl vinyl ether preferring the s-*trans* conformation though there is no obvious steric hindrance for the attainment of the s-*cis* form. This observation has additional significance concerning attempts to explain the origin of the favor of the s-*cis* conformation of methyl vinyl ether: this conformation has no inherent preference, it is favored only because the other planar form, s-*trans*, is destabilized by steric interactions between the Me group and the  $\alpha$  hydrogen of the vinyl group. If this steric hindrance is relieved, which seems to be the case in 1, the s-*trans* form becomes the more favored one.

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