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Reactions of Some Cyclic Ketene Acetals with Maleic Anhydride and Acrylonitrile

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Abstract — The reactions of 9-methyl-4-methylidene-3,5-dioxabicyclo[5.4.0]undecane with maleic anhydride and acrylonitrile were studied by NMR spectroscopy and were found to give 1 : 1 molecular complexes with equilibrium constants of 0.24 ± 0.06 and 0.14 ± 0.04 l mol^{-1}, respectively. Analysis of the calculated (AM1) heats of formation ΔH, differences in the dipole moments $\Delta\mu$, frequencies and intensities of stretching vibrations of the donor and acceptors, and charge distribution showed formation of π–π, mixed π–π-H, and H complexes with partial charge transfer. These complexes can be used in copolymerization of the above monomers.

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The ethylidene moiety in 9-methyl-4-methylidene-3,5-dioxabicyclo[5.4.0]undecane and 2-methylidene-1,3-dioxepane molecules is linked to two oxygen atoms, which is responsible for the high reactivity of these compounds in reactions accompanied by ring opening. 9-Methyl-4-methylidene-3,5-dioxabicyclo-[5.4.0]undecane and 2-methylidene-1,3-dioxepane are fairly stable as compared, e.g., to their five-membered analogs, and they are important for synthesis of polymers [1]. Moreover, the oxygen atoms in some substituted 1,3-dioxepanes can be involved in the formation of H complexes with chloroform and methanol [2]. If a cyclic acetal contains a double C=C bond, both hydrogen bonding and π–π interactions may occur in its mixtures with π acceptors. The complexes thus formed could undergo polymerization along different pathways, and chain growth could be controlled depending on the predominant mechanism. Although the synthesis and application of cyclic ketene acetals were the subjects of numerous studies, their complex formation was almost not studied.

The goal of this study was to examine donor–acceptor interactions of 9-methyl-4-methylidene-3,5-dioxabicyclo[5.4.0]undecane and 2-methylidene-1,3-dioxepane with maleic anhydride and acrylonitrile by experimental (NMR) and theoretical methods (AM1).

Addition of 9-methyl-4-methylidene-3,5-dioxabicyclo[5.4.0]undecane (D_1) to maleic anhydride (MA) or acrylonitrile (AN) leads to downfield shift of signals from protons in the acceptor molecule. The changes in the chemical shifts Δ fit a straight line in the Benesi–Hildebrand coordinates (Fig. 1), indicating formation of 1 : 1 complexes with equilibrium constants of 0.24 ± 0.06 l mol^{-1} (complex $D_1 \cdots MA$) and 0.14 ± 0.06 l mol^{-1} ($D_1 \cdots AN$). As with complexes of maleic anhydride with 2-chlorovinyl ether, tetrahydrofuran, and acetone [3], the observed downfield shift indicates that protons in the maleic anhydride molecule are involved in hydrogen bonding with oxygen atoms in the dioxepane ring.

With the goal of determining the configuration of complexes derived from the above donors and maleic

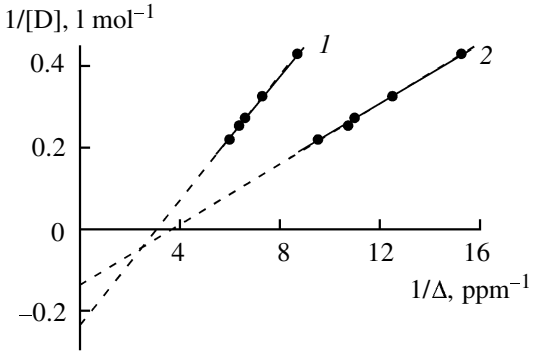

Fig. 1. Plots of the changes in the chemical shifts of protons in (*1*) maleic anhydride and (*2*) acrylonitrile versus concentration of 9-methyl-4-methylidene-3,5-dioxabicyclo[5.4.0]undecane in the Benesi–Hildebrand coordinates.

Table 1. Principal parameters of complexes **I**–**IX** (AM1 calculation)

Comp. no.	$-\Delta H_f^0$, kcal mol^{-1}	$-\Delta H$, kcal mol^{-1}	μ, D	Δμ, D	Charge, a.u.	
					donor	acceptor
I	174.53	1.11	6.21	1.12	0.003	–0.003
II	151.79	1.24	6.18	1.03	0.0035	–0.0035
III	176.47	3.05	4.21	0.42	0.001	–0.001
IV	153.61	3.05	3.40	0.31	0.001	–0.001
V	53.47	1.37	5.07	0.48	0.001	–0.001
VI	30.60	1.37	4.88	0.45	0.001	–0.001
VII	175.61	2.18	2.74	0.35	–0.001	0.001
VIII	52.96	0.85	4.88	0.60	0.002	–0.003
IX	53.70	1.60	1.40	0.35	0.002	–0.002

anhydride (or acrylonitrile), we performed AM1 quantum-chemical calculations [4] (MOPAC 6 software package [5]) of their geometric and electronic parameters. Conformational analysis [6] of donors D_1 and 2-methylidene-1,3-dioxepane (D_2) showed that D_1 molecule is mainly (80%) an isomer with *trans*-junction of the dioxepane (*twist–chair*) and hexane (*chair*) rings and that molecule D_2 adopts a *twist–chair* conformation (by 89%).

The donor and acceptor molecules were moved (Fig. 2) in such a way that their double bonds be closer to each other (complexes **I**, **II**, **V**, and **VI**) or by orienting the carbonyl oxygen atom of maleic anhydride (complexes **III**, **IV**, and **VII**) or 6-H (**VIII**) or 7-H (**IX**) of acrylonitrile toward the dioxepane ring. In the optimized structures of complexes **I** and **II** (Fig. 2a), the double bond planes form a dihedral angle of about 95° and 105°, respectively, and the

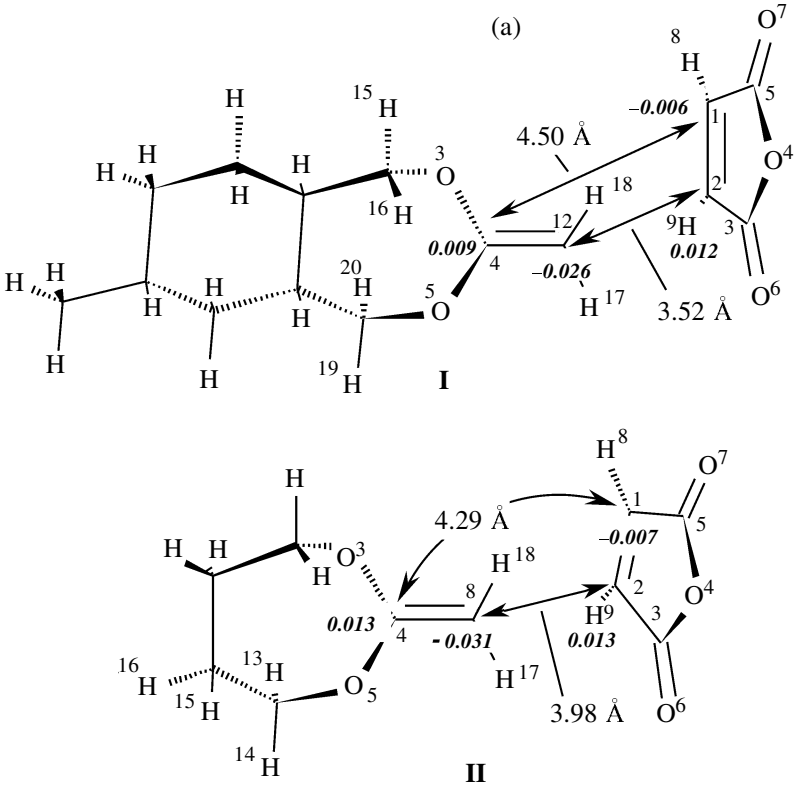

Fig. 2. Optimized structures of complexes formed by 9-methyl-4-methylidene-3,5-dioxabicyclo[5.4.0]undecane (**I, III, V**, and **VII**–**IX**) and 2-methylidene-1,3-dioxepane (**II, IV**, and **VI**) with maleic anhydride (**I**–**IV** and **VII**) and acrylonitrile (**V, VI, VIII**, and **IX**); (a) complexes formed by π–π interactions between the double bonds, (b) complexes formed by π–π interactions and hydrogen bonds, and (c) H complexes. Interatomic distances and changes in the charges on atoms (a.u.) are given.

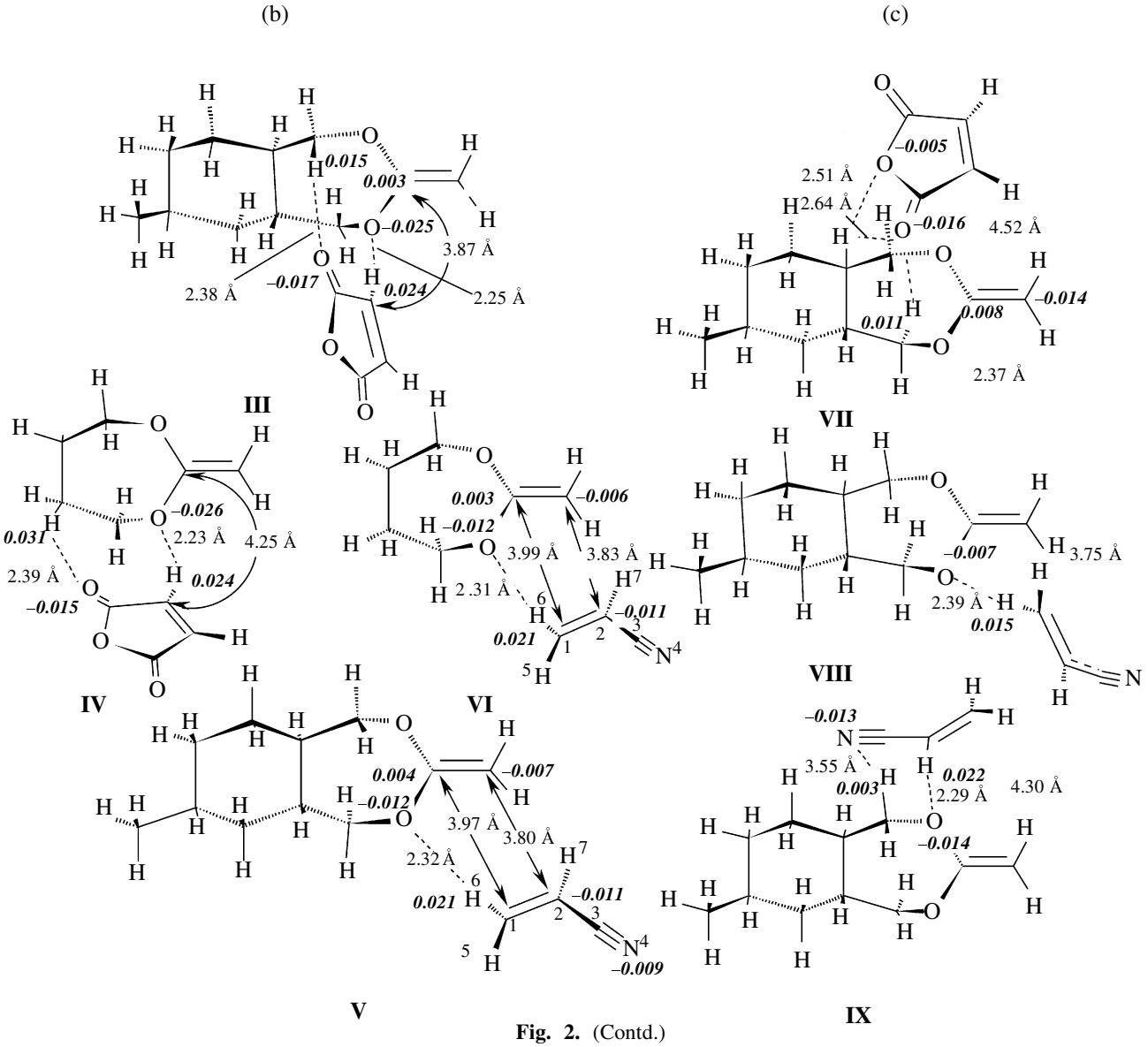

Fig. 2. (Contd.)

distance between these planes is sufficiently short to enable π–π interaction. Complexes **I** and **II** are characterized by relatively large dipole moments (Table 1), and their heats of formation ΔH ($\Delta H = H_{comp} - \Sigma H_{init}$) are 1.11 and 1.24 kcal mol^{-1}, respectively.

In the IR spectra of complexes **I** and **II**, absorption bands due to stretching vibrations of the ketene acetal C=C bond ($\nu_{C=C}$) are displaced by 5 and 4 cm^{-1}, respectively, and their intensity increases by 17 and 30% (Table 2). The band at 1595 cm^{-1}, belonging to $\nu_{C=C}$ of maleic anhydride, does not change its position, but its intensity increases almost twice (Table 2), indicating participation of the double bond of the acceptor in complex formation. The C–H stretching vibration frequency of maleic anhydride (3095 cm^{-1}) changes by 38 and 36 cm^{-1}, and its intensity increases by a factor of 1.6 or 2.2 for complexes **I** and **II**, respectively (Table 2). Therefore, structures **I** and **II** may be regarded as π–π complexes.

Analysis of the electronic parameters showed the presence of a partial charges on the molecules of the donor and maleic anhydride in structures **I** and **II** (Fig. 2a, Table 1), which is consistent with the theoretical views on π–π charge-transfer complexes [7]. In addition, the difference in the charges on the double-bonded carbon atoms of the ethylidene moiety in complexes **I** and **II** increases by 0.035 and 0.044 a.u., i.e., the ketene acetal double bond in the complexes is strongly polarized. The double C=C bond in maleic anhydride is also polarized. The proton in maleic anhydride, nearest to the donor molecule,

Table 2. Stretching vibration frequencies and intensities in the IR spectra of initial compounds and complexes **I**–**IX**

Comp. no.	ν,[a] cm^{-1}		$-\Delta\nu$,[a] cm^{-1}	Intensity A, $km\,mol^{-1}$		A_{comp}/A_{init}	Assignment
	donor or acceptor	complex		donor or acceptor	complex		
VI	3099	3091	8	19.65	18.56	0.94	$=CH_2$ (s)
VIII		3088	11		20.34	1.04	(AN)
V	3100	3085	15	16.05	33.29	2.07	$=C-H^{5,6}$ (as)
VI		3085	15		33.07	2.06	(AN)
VIII		3085	15		24.99	1.56	
V	3099	3091	8	9.20	8.36	0.91	$=C-H^7$
VI		3092	7		8.43	0.91	(AN)
VIII		3094	5		17.59	1.91	
IX		3069	30		42.80	4.65	
I	3095	3057	38	49.06	76.53	1.56	=C–H (as)
II		3059	36		95.67	1.95	(MA)
III		3061	34		97.94	2.00	
IV		3062	33		106.89	2.18	
II	3072	3070	2	36.00	41.04	1.14	$=CH_2$ (s) (D_2)
VI	3050	3046	4	11.23	12.56	1.12	$=CH_2$ (as) (D_2)
I	3050	3049	1	11.04	21.43	1.94	$=CH_2$ (as)
V		3047	3		12.16	1.10	(D_1)
VIII		3045	5		20.76	1.88	
VI	2248	2247	1	2.57	4.34	1.69	C≡N
VIII		2247	1		4.06	1.58	(AN)
IX		2246	2		3.52	1.37	
III	1775	1772	3	308.78	343.73	1.11	C=O
IV		1773	2		329.22	1.07	(MA)
VII		1772	3		294.76	0.95	
II	1664	1659	5	54.87	68.98	1.30	C=C (D_2)
I	1662	1658	4	61.7	72.43	1.17	C=C (D_1)
VII		1661	2		65.79	1.07	
V	1608	1606	2	1.15	2.25	1.96	C=C
VI		1606	2		2.18	1.90	(AN)
VIII		1606	2		2.18	1.90	
I	1595	1594	1	1.65	2.60	1.60	C=C
II		1594	1		2.78	1.72	(MA)
III		1594	1		1.96	1.19	
IV		1594	1		2.10	1.27	

[a] The ν values are given with account taken of the following scaling factors: 3100–2800 cm^{-1} (C–H), 0.95–0.97; 2240–1600 cm^{-1} (C≡N, C=O, C=C), 0.88–90.

acquires a larger positive charge (Fig. 2a), which should enhance the reactivity of molecules in the complex. Change of the torsion angles $C^2O^3C^4O^5$ and $O^3C^4O^5C^6$ by –14.6 and 13.2° (**I**) and –13.9 and 12.6° (**II**) in going from the free molecule to the complex increases strain in the dioxepane ring in complexes **I** and **II** and favors its opening in radical reactions.

The distances between the double bonds in complexes **III**–**VI** (Fig. 2b) and increased intensities of the $\nu_{C=C}$ bands of maleic anhydride and acrylonitrile (Table 2), their position changing only slightly, suggest the possibility for π–π interaction. On the other hand, the O^5 atom in donor D_1 or D_2 is involved in hydrogen bond with proton of maleic anhydride (complexes **III** and **IV**) or 6-H of acrylonitrile (**V**, **VI**), and the carbonyl oxygen atom of maleic anhydride is linked to 15-H of D_1 (**III**) or D_2 (**IV**) (Fig. 2b). As a result, the $\nu_{C=O}$ (1775 cm^{-1}) and ν_{C-H} bands (=CH_2, AN; 3100 cm^{-1}) are displaced, and their intensity increases (Table 2).

If a complex involves two hydrogen bonds, the ΔH value is maximal (Table 1, Fig. 2; complexes **III** and **IV**). Complexes **V** and **VI** are characterized by twice as low ΔH value (Table 2), presumably due to formation of weaker hydrogen bonds or formation of only one H bond; alternatively, the ΔH value is an average of the two kinds of interaction.

Considerable increase in the charges on the oxygen and hydrogen atoms in complexes **III**–**VI** (Fig. 2b) and charge distribution therein suggest an interaction like intermolecular hydrogen bond. As in π complexes **I** and **II**, the difference in the charges on the double-bonded carbon atoms in ketene acetal fragment increases. The donor and acceptor molecules in these complexes acquire a partial charge (Table 1); therefore, they can also be treated as charge-transfer complexes. Since structures **III**–**VI** are characterized by both π–π interactions and H bonding, they may be referred to as mixed type complexes (two kinds of donor–acceptor interactions).

Complexes **VII**–**IX** (Fig. 2c) constitute a specific group. The distances between the 14-H and 19-H protons of donor D_1, on the one hand, and carbonyl and ester oxygen atoms of maleic anhydride, on the other, are quite sufficient for H bonding. This follows, e.g., from displacement of the $\nu_{C=O}$ band and increased absolute charge on 14-H and 19-H of the donor and O^4 and O^6 of the acceptor. The position of the $\nu_{C=C}$ band of the donor changes insignificantly (by 2 cm^{-1}; Table 2, complex **VII**), as well as the charges on the double-bonded carbon atoms, due to orientation of the maleic anhydride molecule in the complex.

The 6-H and 7-H protons of acrylonitrile in complexes **VIII** and **IX** (Fig. 2c) are linked to the dioxepane oxygen atoms O^5 and O^3, and the nitrogen atom either does not participate in complex formation (structure **VIII**) or forms hydrogen bond with the 15-H hydrogen atom in the ring (**IX**). The latter assumption may be valid, taking into account that ΔH of **IX** is larger than ΔH of complex **VIII** having one hydrogen bond (Table 1). Hydrogen bonding leads to displacement of the bands at 3100 and 3099 cm^{-1} by 15 and 30 cm^{-1}, respectively (Table 2). Complex **VI** also showed in the IR spectrum increased intensity of the $\nu_{C\equiv N}$ band and its slight displacement (Table 2). Presumably, this is the result of conjugation in the acrylonitrile molecule within the complex. Moreover, increase in the negative charge on the nitrogen atom (by 0.013 a.u.) in complex **IX**, was revealed, which may be due to its participation in hydrogen bonding. Taking into account variation of charges on O^5 and 6-H in **VIII** and on O^3 and 7-H in **IX** we believe that hydrogen bond between these atoms is actually formed. Such complexes are characterized by relatively small $\Delta\mu$ values (e.g., structures **III**–**IX**; Table 1, Fig. 2b) as compared to **I** and **II** where only π–π interaction occurs. A probable reason is mutual compensation of dipole moments via polar electrostatic interactions between the donor and acceptor upon hydrogen bonding. As follows from analysis of the $\Delta\mu$ and ΔH values (Table 1) for complexes **I**–**VI** (Fig. 2) with similar mutual orientation of the donor and acceptor components but different structure of the ketene acetal fragment, the hexane ring fused in the *trans* mode to the dioxepane ring almost does not affect the stability and polarity of the complexes.

Thus, the determined equilibrium constants reflect the overall process of formation of different kinds of complexes between donors D_1 and D_2 and maleic anhydride and acrylonitrile. The results of calculation suggest formation of π–π, mixed π–π-H, and H complexes. Presumably, the examined supramolecular π–π structures are characterized by considerable polarization of the double bonds in both donor and acceptor; therefore, they could exhibit high reactivity in radical processes and favor introduction of ketene acetal fragments into both hetero- and homopolymeric chains. Mixed complexes involving two kinds of donor–acceptor interactions should accelerate opening of the dioxepane ring with formation of oligomeric products. The third type of supramolecular structures, H complexes are likely to be capable of participating only in generation of initiating species.

EXPERIMENTAL

The synthesis and properties of 9-methyl-4-methylidene-3,5-dioxabicyclo[5.4.0]undecane were described in [8]. Acrylonitrile was distilled just before use; it contained no less than 99.97 wt% of the main substance. Maleic anhydride was purified by double sublimation.

The ^1H NMR spectra were recorded on a Gemini-200 instrument (200 MHz) from solutions in carbon tetrachloride using Me_4Si as internal reference; the concentration of maleic anhydride and acrylonitrile was maintained at 0.05 M, and the concentration of donor D_1 was varied from 2.02 to 4.28 M. The error in the determination of chemical shifts was ±0.0025 ppm.

The equilibrium constant K_{eq} was determined using the Benesi–Hildebrand equation [3]:

$$\frac{1}{[D]_0} = \Delta_c K_{eq} \frac{1}{\Delta} - K_{eq}.$$

Here, $\Delta = (\delta_{obs} - \delta_0)$ is the observed change in the chemical shifts of protons in an acceptor in the presence of a donor, Δ_c is the difference in the chemical shifts of protons in the acceptor molecule within the complex and in the free state, and $[D]_0$ is the donor concentration.

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