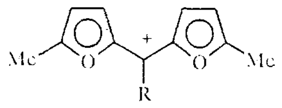
POLYFURYL(ARYL)ALKANES AND THEIR DERIVATIVES.
6.* STEREOCHEMISTRY OF INTRAMOLECULAR ROTATIONS ABOUT THE C—C$^+$ BONDS IN ARYL(ALKYL)DIFURYLCARBONIUM IONS

A. V. Butin, G. D. Krapivin, V. G. Kul'nevich,
E. V. Vorontsov, and V. I. Bakhmutov

It was demonstrated by dynamic ^1H NMR spectroscopy that for difurylmethyl and gem-difurylethyl cations conformational changes are realized through rotation of one of the furan rings, whereas in the case of aryldifurylmethyl cations conformational transformations take place as the simultaneous rotation of two aromatic rings; the correlated rotation of the two furan rings proceeds with smaller energy expenditures.

The interest in the stereochemistry of triarylmethyl cations is due to the unusual chirality of these molecules that arises due to the existence of propeller conformations [2, 3]. The realization of such conformations is ensured by two opposing effects: the steric repulsion of the ortho protons or the ortho substituents of the aromatic rings and the striving of the rings to situate themselves in the trigonal plane of the cation center for delocalization of the positive charge. As a rule, the conformational stability of the cations is low, and the enantiomers are readily interconverted on the NMR time scale [2, 4, 5]. Thus the NMR spectra make it possible to not only observe the enantiomers but also to investigate the kinetics of their stereochemical transformations.

In addition to optical isomers, the development of diastereomeric structures, which have also been detected and investigated intensively by NMR spectroscopy, is also possible for o- and m-substituted derivatives of triarylmethyl cations [3, 6]. The previously synthesized [1] perchlorates Ia-h are compounds of this type, and the study of their stereochemical flexibility as a function of the electronic properties of R and the substituent in the benzene ring by dynamic NMR spectroscopy is therefore of definite interest.



I a R = H; b R = Me; c R = 4-BrC$_6$H$_4$; d R = 4-ClC$_6$H$_4$; e R = Ph; f R = 4-CH$_3$C$_6$H$_4$; g R = 4-CH$_3$OC$_6$H$_4$; h R = 4-HOC$_6$H$_4$

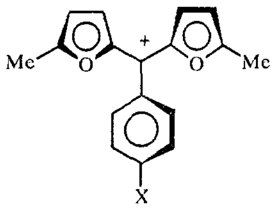
For aryl-substituted cations Ic-h one may a priori expect the existence of enantiomeric structures of the A and B type. In fact, according to the results of x-ray diffraction analysis [1], the furan rings of the trifurylmethyl cation deviate 10° from the plane of the carbonium-ion center. Unfortunately, because of the absence of the corresponding diastereotropic rings in the

---

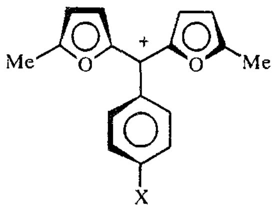
*For Communication 5 see [1].

Krasnodar Polytechnical Institute, Krasnodar 350072. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 450-455, April, 1993. Original article submitted June 22, 1992.

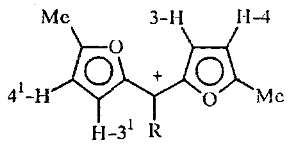
Ic-h molecules (the ortho and meta protons of the aromatic rings are not diastereotropic), it is not possible to form a judgment regarding the presence of forms A and B and their interconversions from the NMR spectra. At the same time, diastereomeric structures C, D, and F should be different in the ^{1}H NMR spectra.



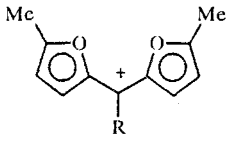
A



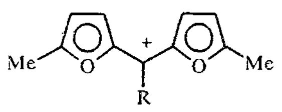
B



C



D



F

As it turned out, the ^{1}H NMR spectra of Ia-h in CD_2Cl_2 or $C_6D_5NO_2$ depend on the temperature [1]. Thus, for example, at 200 K in the ^{1}H NMR spectrum of cation Ic in CD_2Cl_2 one observes two sets of signals, in one of which nonequivalence of all of the protons of the furan rings (8.57, 7.40, 6.97, and 6.75 ppm), as well as the CH_3 groups (2.50 and 2.62 ppm), is manifested. The second set contains one signal of equivalent CH_3 groups (2.65 ppm) and two signals of furan protons of the AB type (7.45 and 6.81 ppm). An increase in the temperature of the solution to 248°K leads to selective broadening of the signals of the first set, which also makes it possible to make the above-cited assignments. A similar spectral pattern is observed in all of the investigated cases, and, consequently, of the three possible diastereomeric structures of cations Ia-h, only two appear in the PMR spectra. Because of the pronounced steric repulsion of the furan protons in the 3 position, structure F for all substituents R should be expected to be the least thermodynamically stable. Then, postulating that precisely this structure is not recorded in the ^{1}H NMR spectra because of its small population and also taking into account the fact that the chemical shifts of the protons in the 3 (3′) and 4 (4′) positions in structure D should be close to the chemical shifts of the protons in the 3′ and 4′ positions in structure C, the corresponding spectral assignments (Table 1) are easily made for the investigated cations.

It follows from the integral intensities of the lines that the ratio [C]/[D] of the populations of the conformations of the Ia, c-h cations is virtually the same as the statistical value and is equal to two. Thus in this case, despite the substantial change in the nature of R (transition from R = H to R = Ar), energy differences between structures C and D are not observed. This result once again constitutes evidence for the realization of propeller conformations in solutions of ions Ia, c-h. The proportion [C]/[D] significantly changes only in passing to $R{=}CH_3$. Here, the [C]/[D] ratio is equal to five. It appears that $CH_3 \ldots H(3)$, H(3′) steric contacts begin to play a significant destabilizing role in the case of the sterically isotropic CH_3 group.

According to modern concepts, the positive charge of aryl-substituted carbonium ions is stabilized by p,π-interaction of the cation center and the aromatic ring. This interaction leads to an increase in the double-bond character of the $C^+-C_6H_4X$ fragment and the development of a hindered-rotation effect [3]. In addition, steric interactions of the ortho protons and ortho substituents also play a large role in the development of hindered rotation in the case of triarylmethyl cations [3]. The latter is clearly exhibited for solutions of triarylmethanes [7]. It is now generally accepted that rotations about the $C^+-C_6H_4X$ bonds of triarylmethyl cations and of $C-C_6H_4X$ bonds of triarylmethanes are correlated and proceed as simultaneous rotation of two aromatic rings [7]. Then, for cations Ic-h one might expect the following spectrally distinguishable movements: simultaneous conrotatory rotation of two furan rings with orientation of the benzene ring in the trigonal plane of

TABLE 1. Spectral Parameters of Cations Ia-h in CD_2Cl_2

Compound	Structure	Chemical shifts, δ, ppm						T, K
		3'-H	4'-H	3-H	4-H	R	CH_3	
I a[*]	C	8,05	6,85	8,25	6,95	7,63		300
	D	8,04	6,85	8,04	6,85	7,71		
I b	C	8,05	6,73	8,47	6,87	2,65	2,52[2*]	300
	D	8,10	6,75	8,10	6,75	2,65	2,60	
I c	C	7,40	6,75	8,57	6,97	7,58 7,32	2,52	200
	D	7,45	6,81	7,45	6,81	7,58 7,32	2,65	
I d	C	7,60	6,90	8,75	7,10	7,60[3*]	2,60 2,70	230
	D	7,60	6,95	7,60	6,95	7,60[3*]	2,75	
I e	C	7,60	6,75	8,60	6,98	7,45[3*]	2,55 2.63	220
	D	7.60	6,80	7,60	6,80	7,45[3*]	2,66	
I f	C	7,45	6,75	8,60	6,98	7,25[3*]	2,50 2,60 2,32[4*]	200
	D	7.40	6,77	7,40	6,77	7,25[3*]	2,62 2,32[4*]	
I g	C	7.43	6,75	8,72	6,88	7,50 6,95	2,48 2,54 3,77[4*]	200
	D	7,43	6,76	7,43	6,76	7,50 6,95	2,58 3,77[4*]	
I h	C	7,13	6,70	8,15	6,80	7,45 7,07	2,52 2,61	200
	D	7,13	6,70	7,13	6,70	7,45 7,07	2,57	

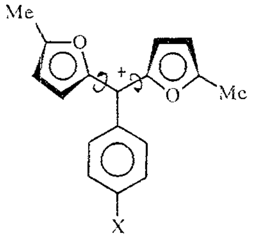
[1*] In $C_6D_5NO_2$.

[2*] In CD_2Cl_2 the shifts of the CH_3 groups in conformer C coincide but differ in $C_6D_5NO_2$ (2.45; 2.50 ppm).

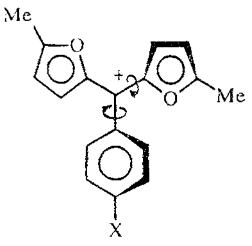
[3*] Center of a multiplet.

[4*] Signals of the CH_3 and CH_3O groups of the benzene ring.

the cation center (mechanism 1) and simultaneous rotation of the furan and benzene rings with orientation of the other furan ring in this plane (mechanism 2). For structure C the realization of only mechanism 1 leads to averaging of the 5-CH_3 signals of this conformation. Mechanism 2 ultimately leads to the conversion of C to D and, consequently, to averaging of all of the 5-CH_3 lines.



Mechanism 1



Mechanism 2

As we have already reported above, the ^1H NMR spectra of cations Ic-h depend on the temperature, attesting to conformational transitions on the ^1H NMR time scale; a substantial difference in the rates of averaging of the CH_3 signals in conformation C (mechanism 1) and averaging of these signals between structures C and D (mechanism 2) is observed in the case of cation Ic in CD_2Cl_2 (Fig. 1).

TABLE 2. Kinetic and Thermodynamic Parameters of the Conformational Transformations of Cations Ia-h in CD_2Cl_2

Compound	$\ln(k_1)$*	$\ln(k_2)$	$\Delta G^{\#}_{298}$ (1),** kJ/mole	$\Delta G^{\#}_{298}$ (2), kJ/mole	$\Delta G^{\#}_{298}$ (2) $-\Delta G^{\#}_{298}$ (1), kJ/mole
Ia			82,0***	82,0	0,0
Ib			68,2***		
Ic	2,263	4,382	60,6	62,7****	
Id	2,313	5,360	60,6	61,1	0,5
Ie	2,526	4,779	61,5	62,0	0,5
If	3,370	6,225	56,5	58,5	2,0
Ig	6,530	6,502	48,9	57,7	8,8
Ih	11,331	8,468	32,6	53,1	20,5

---

*Found by calculation of the form of the lines of the CH_3 signals for the investigated cations at one temperature: T = 257 K and T = 303 K for ln (k_1) and ln (k_2), respectively.

**The $\Delta H^{\#}$ and $\Delta S^{\#}$ values, which were used to calculate $\Delta G^{\#}$ as the most accurate thermodynamic parameter, were found from the dependences of ln (kT) on 1/T; the accuracy in the determination was ± 0.9 kJ/mole.

***In $C_6D_5NO_2$.

****Determined at T = 303 K.

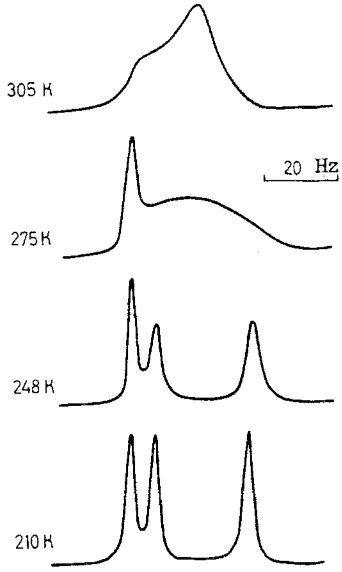


Fig. 1. Temperature dependence of the experimental PMR spectra of Ic in CD_2Cl_2.

The experimentally found kinetic parameters of processes 1 and 2 are presented in Table 2, where k_1 and k_2 are the rate constants of averaging of the CH_3 signals in conformation C (mechanism 1) and of the conversion of C to D (mechanism 2), respectively. It follows from Table 2 that the rate of stereochemical transformation 1 depends on the nature of substituent X in the benzene ring and is described by correlation equation (1); this constitutes evidence for a sharp decrease in the energy barrier with an increase in the electronic properties of substituent X.

$$\ln(k_1) = (-9{,}02 \pm 1{,}4)\,\sigma^+ + (2{,}18 \pm 0{,}63) \tag{1}$$

Generally speaking, substituent X in the benzene ring may have an effect both in the ground state and in the transition state of the investigated molecules. In the ground state of the propeller conformations an increase in the donor properties of X should promote stabilization of the positive charge of the carbonium-ion center by the benzene ring, thereby leading to a decrease in the order of the bonding of the positively charged carbon atom with the furan rings. In the transition state of concerted rotation 1 both furan rings are perpendicular to the trigonal plane of the carbonium-ion center, while the benzene ring lies in this plane. It is clear that the presence of a donor substituent in the benzene ring in this sort of orientation will substantially decrease the energy of the transition state. Thus the effect of the substituent is evident in both the ground state and in the transition state of correlated rotation 1, and this is experimentally observed.

Movement 2 leads to deviation of one of the furan rings and the benzene ring from the plane of the carbonium-ion center. It is therefore reasonable to assume an increase in the steric factor (the larger size of the benzene ring as compared with the furan ring) and a decrease in the effect of substituent X on the energy of the transition state, since this effect is retained only in the transition state. In this connection, movement 2 should be less rapid and susceptible to a lesser extent to the effect of substituent X. It is apparent from Table 2 that the assumptions stated above are in complete agreement with reality: the rate of conformational transitions increases with an increase in the donor capacity of the benzene ring; however, this dependence is less pronounced quantitatively [Eq. (2)]. The fact that the differences in the energy parameters of processes 1 and 2 decrease on passing in the series of substituents from X = OH to X = Cl is also in agreement with the information set forth above.

$$\ln(k_2) = (-3{,}58 \pm 0{,}71)\ \sigma^{+} + (4{,}94 \pm 0{,}32) \tag{2}$$

The participation of the benzene ring in the conformational transitions of the investigated compounds is also confirmed independently by the substantial increase in the $\Delta G^{\#}$ parameter on passing from aryl-substituted cations to cations Ia, b (Table 2).

In contrast to arylmethyl cations Ic-h, the rates of averaging of the CH_3 signals of conformation C and averaging of these signals on conversion of rotamer C to D for cations Ia are virtually equal to one another. It is fully likely that, as in the case of diarylmethanes [7], concerted movement is not required here. Then, the rotation of one of the furan rings in structure C leads to averaging of the 5-CH_3 signals of this structure and simultaneously to the conversion of form C to D (as in the previously described cases, structure F is not observed here). In examining the conformational transitions of cation Ia as a result of rotation of one furan ring about the C^{+}—$C_{(2)}$ or C^{+}—$C_{(2')}$ bond, when R = H is replaced by CH_3 one should expect a decrease in $\Delta G^{\#}$ due to an increase in the stabilization of the positive charge in the transition state. It is apparent from the data obtained (Table 2) that this effect is manifested clearly on passing from Ia to Ib.

In concluding our discussion of the stereochemical flexibility of cations Ia-h we can briefly summarize the results obtained: 1) the rate and mechanism of the diastereomeric transformations of the cations depend on the nature of substituent R; 2) the conformational transformations of cations Ia, b are realized as a result of rotation of one of the furan rings and are accelerated on passing from R = H to R = CH_3 due to better stabilization of the positive charge; 3) the conformational transformations of aryl-substituted cations Ic-h proceed as concerted rotation of two aromatic rings; the synchronous rotation of two furan rings requires the smallest energy expenditures.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded with a Bruker WP-200 SY spectrometer; the temperature of the samples was maintained with an accuracy of ±0.5°C. The calculation of the form of the lines of the NMR signals found in the state of positional exchange in order to determine the lifetime (τ) of the magnetically nonequivalent states of the investigated molecules was carried out by means of the DNMR5 program [8, 9]. The error in the determination of τ was ± 5%. The rate constants of the conformational transitions were assumed to be equal to $1/\tau$, just as for ordinary monomolecular processes.

The σ^{+} constants were taken from [10], and the correlation coefficients for Eqs. (1) and (2) were 0.954 and 0.929, respectively. Compounds Ic-h were obtained by the method in [1].

REFERENCES

1. A. V. Butin, V. G. Kul'nevich, V. T. Abaev, N. G. Mikhailyuchenko, A. V. Shpakov, O. Yu. Okhlobystin, V. E. Zavodnik, and A. I. Lutsenko, Khim. Geterotsikl. Soedin., No. 3, 329 (1993).
2. N. C. Deno, P. T. Groves, and G. Saines, J. Am. Chem. Soc., **81**, 5790 (1959).
3. J. W. Rakshis, J. S. V. McKinley, and H. H. Freedman, J. Am. Chem. Soc., **93**, 6522 (1971).
4. K. Colter, I. I. Schuster, and R. J. Kurland, J. Am. Chem. Soc., **87**, 2278 (1965).
5. K. Colter, I. I. Schuster, and R. J. Kurland, J. Am. Chem. Soc., **90**, 4679 (1968).
6. R. Breslow, L. Kaplan, and D. LaFollette, J. Am. Chem. Soc., **90**, 4056 (1968).
7. M. Oki, Application of Dynamic NMR Spectroscopy to Organic Chemistry, VCH Publishers (1985).
8. G. Binsh, Topics Stereochem., **3**, 97 (1968).
9. L. M. Jackman and F. A. Cotton, Dynamic NMR Spectroscopy, Vol. 2, Academic Press, New York (1975), p. 156.
10. H. C. Brown and Y. Okamoto, J. Am. Chem. Soc., **80**, 4679 (1958).