Molecular Orbital Calculation on 1,2-Difuryl- and 1,2-Dithienyl-ethylenes and Their Photocyclisation Products the Benzodifuranes and Benzodithiophenes

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Es werden die HMO-Berechnungen der 1,2-Difuryl- und 1,2-Dithienyl-äthylene sowie die bei der photochemischen Cyclodehydrierung dieser Verbindungen entstehenden Benzodifurane und Benzodithiophene mitgeteilt. Die chemische Reaktivität dieser Verbindungen wird an Hand der berechneten Reaktivitätsindizes vorausgesagt.

During the last year a series of publications has dealt with the photochemistry of 1,2-difuryl- and 1,2-dithienyl-ethylenes¹⁻³. These compounds undergo photochemical *cis-trans* isomerization¹ as well as

E_{π} = total π -energy for the ground state. E_{π}^* = total π -energy for the excited state.

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¹ C. M. ORLANDO, A. A. ZIMMERMAN, M. H. GIANNI, and K. WEISS, J. org. Chemistry, in press.

² R. M. KELLOGG, M. B. GROEN, and H. WYNBERG, J. org. Chemistry **32**, 3093 [1967]; H. WYNBERG and M. B. GROEN, J. Amer. chem. Soc. **90**, 5339 [1968].

³ C. E. LOADER and C. J. TIMMONS, J. chem. Soc. [London] (C) **1967**, 1677.

1,2-Di-(3-furyl)-ethylene

Benzo[1,2-b:4,3-b']-difuran

1,3-Di-(2-thienyl)-ethylene

Benzo[2,1-b:3,4-b']-dithiophene

1,2-Di-(2-furyl)-ethylene

Benzo[1,2-b:4,3-b']-difuran

1,2-Di-(2-thienyl)-ethylene

Benzo[1,2-b:4,3-b']-dithiophene

photocyclisation^{2,3}. In presence of oxidizing agents 1,2-dithienyl-ethylenes yield benzodithiophenes². Similarly 1,2-di-(2-furyl)-ethylene results benzo[1,2-b:4,3-b']-difuran³.

By means of this photocyclodehydrogenation the unsubstituted compounds of benzodifuranes and benzodithiophenes which besides the benzo[1,2-b:4,3-b']-dithiophene⁴ are unknown, are now available.

The present communication reports a theoretical study of some 1,2-difuryl- and 1,2-dithienyl-ethylenes in order to get some information about the mechanism of the photocyclisation. Furthermore we report the reactivity indices of the benzodifuranes and benzodithiophenes regarding substitution reactions as to predict the positions of electrophilic, nucleophilic and radical attack.

Theoretical Approach

In general the photocyclisation of 1,2-difuryl- and 1,2-dithienyl-ethylenes produces six possible isomers of benzodifuran as well as benzodithiophenes. From chemical argumentations accompanying the photocyclisation only the following isomers should be stable compounds: benzo[1,2-b:3,4-b']-difuran (**1**) and -dithiophene (**1a**), benzo[1,2-b:4,3-b']-difuran (**2**) and -dithiophene (**2a**) and the benzo[2,1-b:3,4-b']-difuran (**3**) and -dithiophene (**3a**). To these six molecules and the corresponding three difuryl- and dithienyl-ethylenes we applied the MO-theory within the framework of the Hückel method⁵. The assumption was made that all investigated molecules are planar. The empirical parameters used in the calculation are shown in table I.

A similar choice of parameter has been given by SAPPENFIELD and KREEVOY⁶ for furan and thiophene. We calculated the π -bond orders, the π -electron densities, the free valence indices and the total π -energy of the molecules for the ground and the excited state. The results are presented in the molecular diagrams showing the starting 1,2-disubstituted ethylene and the resulting photocyclodehydrogenation product. All numbers in brackets refer to the excited state. The charge densities are multiplied by 1000. The numbers at the end of the arrows represent the free valence indices. For the seek of simplicity the numbering of the atoms in our skeletal structures is somewhat different. We always count the ethylenic carbon atoms in the difuryl- and dithienyl-ethylenes as 1 and 2, the heteroatom in the rings as 3 and 8 respectively, and the numbering of the remaining ring carbon atoms is going clockwise upward. The same numbering is applied to the photocyclodehydrogenation product.

Discussion

The mechanism of the photocyclisation reaction of *cis*-stilbenes is not completely cleared as yet⁷⁻⁹. Several authors assume that the photochemical part of the reaction proceeds from the excited state of the *cis*-compound to the ground state of the cyclisation product⁷⁻⁹. An other discussed mechanism suggests that the photochemical ring closure proceeds via vibrationally excited ground state levels of the *cis*-compound which are reached in a fast $S_1 \rightarrow S_0$ -deactivation process from the short living excited singlet state of the *cis*-compound (Lewis-mechanism)¹⁰. In a study of the photocyclisation

	Ethylene-1,2-di-		Benzodi-	
	-furanes	-thiophenes	-furanes	-thiophenes
α_1	$\alpha + 0.02 \beta$	$\alpha + 0.02 \beta$	α	α
α_x^*	$\alpha + 1.72 \beta$	$\alpha + 0.93 \beta$	$\alpha + 1.72 \beta$	$\alpha + 0.93 \beta$
α_4	α	α	α	α
α_5	$\alpha - 0.04 \beta$	$\alpha - 0.02 \beta$	$\alpha - 0.04 \beta$	$\alpha - 0.02 \beta$
β_{12}	1.02β	1.02β	All resonance integrals in the resulting benzene ring are equal to β	
$\beta_{1 \text{ (ring)}}$	0.54β	0.60β		
β_{34}	0.76β	0.50β	0.76β	0.50β
β_{56}	0.59β	0.64β	0.59β	0.64β

Table I. Resonance and Coulomb Integrals. * x=heteroatom.

⁴ D. S. RAO and B. D. TILAK, J. Sci. ind. Res. [New Delhi] Sect. B **16**, 65 [1957]; C. A. **51**, 13841 [1957].

⁵ E. HÜCKEL, Z. Physik **70**, 204 [1931].

⁶ D. S. SAPPENFIELD and M. KREEVOY, Tetrahedron [London] **19** (Suppl. 2), 157 [1963].

⁷ F. R. STERMITZ, in: O. L. CHAPMAN's "Organic Photochemistry I", M. Dekker Inc., New York 1967, p. 247.

⁸ K. A. MUSZKAT and E. FISCHER, J. chem. Soc. [London] (B) **1967**, 662.

⁹ M. SCHOLZ, F. DIETZ, and M. MÜHLSTÄDT, Z. Chem. **7**, 329 [1967].

¹⁰ H. GÜSTEN and L. KLASINC, Tetrahedron [London] **24**, 5499 [1968].

of *para*- and *meta*-substituted *cis*-stilbenes we were able to show that the quantum yield of the photocyclisation¹¹ is going linear with a reactivity index q_{rs} , being the product of the electron densities of the reacting *o,o'*-positions in the ground state¹⁰. Applying this criterion to the photocyclisation of the difuryl- and dithienyl-ethylenes i.e. multiplying the excited and ground state π -electron densities of the reacting positions we obtain the following results.

	<i>cis</i> -1*	<i>cis</i> -1a	<i>cis</i> -2	<i>cis</i> -2a	<i>cis</i> -3	<i>cis</i> -3a
q_{rs}^*	1.041	1.087	1.132	1.115	0.970	1.092
q_{rs}	1.085	1.086	1.184	1.145	0.994	1.032

Table II. q_{rs} -values for difuryl- and dithienyl-ethylenes.

The q_{rs}^* - and q_{rs} -values predict a photocyclisation probability in the order of *cis*-2 > *cis*-2a > *cis*-3a > *cis*-1a > *cis*-1 > *cis*-3 and *cis*-2 > *cis*-2a > *cis*-1a > *cis*-1 > *cis*-3a > *cis*-3, respectively. According to the experimental data^{2,3} the *cis*-2-, *cis*-1a, *cis*-2a- and *cis*-3a-compounds undergo photocyclisation. With the exception of 3a the oxidation products 2a (90%), 2 (24%) and 1a (47%) have been isolated^{2,3} (yield in parenthesis). In *cis*-3a the abstraction of hydrogen leads to a β -thio-substituted radical which undergoes very rapid elimination of the sulfur as thiyl radical **. From our theoretical data we can expect that 1 can be obtained by photocyclodehydrogenation and 3 probably not. On the contrary to the HMO-calculations for the photocyclisation of mono-substituted *cis*-stilbenes¹⁰ the results of the HMO-calculation for the photocyclisation of 1,2-difuryl- and dithienyl-ethylenes give no distinction whether the photocyclisation proceeds via the excited or the ground state of the *cis*-compound. Although the predicted

order of the q_{rs} -values (ground state) fits better the experimental data than the q_{rs}^* -values, we feel that the small differences between the q_{rs} - and q_{rs}^* -values do not permit a discrimination on the mechanism of the photocyclisation.

In predicting the chemical reactivities shown in table III we have followed the isolated molecule approximation¹² from which we can expect a correla-

Compound	Electrophilic	Nucleophilic	Radical
1	6, 11 > 2*	12, 7 > 1	6 $\geq$ 7, 11, 12
2	5, 11 > 1, 2	4, 12 > 1, 2	4, 12 $\geq$ 5, 11
3	6, 10 > 1, 2	7, 9 > 1, 2	6, 10 $\geq$ 7, 9
1a	6, 11 > 2	12 $\geq$ 7 > 1	12, 7 > 6
2a	5, 11 > 1, 2	4, 12 > 1, 2	4, 12 > 5, 11
3a	6, 10 > 1, 2	7, 9 > 1, 2	7, 9 > 6, 10
<i>cis</i> -1	6 $\geq$ 11 > 10	4 > 12 > 7	1, 2 > 4
<i>cis</i> -2	5, 11 > 6, 10	4, 12 > 1, 2	1, 2 > 4, 12
<i>cis</i> -3	6, 10 > 1, 2	4, 12 > 7, 9	1, 2 > 4, 12
<i>cis</i> -1a	6 $\geq$ 11 > 10	1 > 4 > 2, 12	1 > 2 > 4
<i>cis</i> -2a	5, 11 > 6, 10	1, 2 > 4, 12	1, 2 > 4, 12
<i>cis</i> -3a	6, 10 > 7, 9	1, 2 > 4, 12	1, 2 > 4, 12

Table III. The Prediction of Chemical Reactivity Based on Charge Densities and Free Valence Indices. * The numbers refer to the numbers in the skeletal structures.

tion between the electron densities and the attacking charged species. For radicals the correlation with the free valence proved to be successful. The most reactive position in benzodifuranes and benzo-dithiophenes is generally in the five membered rings. In the difuryl- and dithienyl-ethylenes this position tends to be on the ethylenic double bond (especially for radical attack). Although not much synthesis has been done on these molecules as yet the available results support our predictions^{4,13-17}.

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* *cis*-1 is the corresponding 1,2-disubstituted ethylene yielding 1 on photocyclodehydrogenation.

** see ² and papers cited there.

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¹³ Derivatives of benzo[1,2-b:3,4-b']-difuran: T. TOMINAGA, J. pharmac. Soc. Japan [Yakugakuzasshi] **76**, 1385 [1956]; G. R. KELKAR and D. B. LIMAYE, Rasayanam [J. Progr. chem. Sci.] **1**, 228 [1943]; C. A. **36**, 1037 [1942]; D. B. LIMAYE and V. V. NAGARKAR, ibid. **1**, 255 [1943]; C. A. **38**, 4264 [1944].

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¹⁵ Derivatives of benzo[2,1-b:3,4-b']-difuran: R. ROYER, J. L. DEROCQUE, P. DEMERSEMAN, and A. CHENTIN, C. R. Ser. C, **262**, 1286 [1966]; W. LIMONTSCHW and E. WIESENBERGER, Mh. Chem. **83**, 137 [1952]; O. DISCHENDORFER and W. LIMONTSCHW, ibid. **80**, 741 [1949].

¹⁶ Derivatives of benzo[1,2-b:3,4-b']-dithiophene: D. S. RAO and B. D. TILAK, J. sci. ind. Res. [New Delhi] Sect. B **13**, 829 [1954]; C. A. **50**, 934 [1956].

¹⁷ Derivatives of benzo[2,1-b:3,4-b']-dithiophene: D. S. RAO and B. D. TILAK, J. sci. ind. Res. [New Delhi] Sect. B **17**, 260 [1958]; C. A. **55**, 22282 [1961].