QUANTUM-CHEMICAL STUDY OF THE HYDRIDE LABILITY OF HYDROGEN IN THIAPYRANS AND RELATED COMPOUNDS

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A method is proposed for the quantitative evaluation of the relative hydride lability of hydrogen in a number of compounds from the hydride ion affinity of the corresponding cations. The relative labilities of H^- in 4H- and 2H-thiapyrans, 4H- and 2H-pyrans, 2H-thiapyran 1,1-dioxide, cyclopentadiene, and cycloheptatriene were determined by the CNDO/2 (complete neglect of differential overlap) method. It is shown that the thiapyran and pyran heterorings are distinguished by high hydride lability of hydrogen; this is evidently the principal reason for their ability to undergo disproportionation. It was established that cycloheptatriene should be a more active hydride-ion donor in nonpolar media. Correlation of the acidities of the examined compounds with the proton affinity of the corresponding anions, calculated by the CNDO/2 method, was noted.

Substituted 4H-thiapyrans undergo disproportionation in the presence of protic acids to give a mixture of the corresponding thiacyclohexanes and thiapyrylium salts [1]. The proposed reaction mechanism for disproportionation includes a step involving hydride-ion migration from 4H-thiapyran to the heteroring with a protonated double bond, i.e., rather high hydride lability of the hydrogen attached to the γ-carbon atom of the 4H-thiapyran ring is assumed. The fact that sym-octahydrothiaxanthene is one of the most active hydride-ion donors among heterocyclic compounds [2] confirms the correctness of this assumption. Disproportionation is also characteristic for pyrans, although the pyran ring is less inclined to give up a hydride ion [3].

In order to ascertain the extent of the H-donor properties of the indicated heterocycles and whether other similar compounds are capable of undergoing some degree of disproportionation in protic acids, it is necessary to make a quantitative evaluation of the hydride lability of hydrogen in various compounds. There are presently no experimental methods for the evaluation of this quantity [4]. However, the change in the hydride lability in a series of HX compounds can be predicted by comparison of the hydride-ion affinities of X^+ cations produced in the hypothetical dissociation $HX \rightarrow X^+ + H^-$. The existence of a linear correlation of the acidities of protic acids and the proton affinities [5] of the corresponding anions X^- may serve as a basis for this sort of assumption. The difference in the energies of the acid and the corresponding anion ($\Delta E = E_X^- - E_{HX}$) was calculated for the gas phase by the standard CNDO/2 (complete neglect of differential overlap) method with automatic optimization of the bond lengths.

The aim of the present research was to make a quantitative evaluation of the relative hydride lability of hydrogen in thiapyrans (I), pyrans (II), 2H-thiapyran 1,1-dioxide (III), cyclopentadiene (IV), and cycloheptatriene (V) from the $\Delta E_+ = E_X^+ - E_{HX}$ values by the CNDO/2 method. The experimental values of the geometrical parameters were taken for compounds III [6], IV [7], and V [8], and the remaining molecules and ions were calculated with the standard bond lengths. The bond lengths were not optimized, since the values obtained in [5] are close to the standard values.

Because of the complexity of the compounds examined in this research and the absence of optimization of the geometry, the existence of a correlation of their acidities with the calculated ΔE_- values should have been verified initially. It is difficult to expect a good linear pK_a (ΔE_-) dependence for the examined compounds, since, on the one hand, the CNDO/2 method rather poorly reproduces the energies of formation of molecules [9] and, on the other, the acidities were determined for substituted compounds (and extremely approximately in most cases) by the use of different bases. Nevertheless, the pK_a values for the examined rings and the theoretical evaluation of the proton affinity of the anions are in good agreement and increase symbatically in the

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TABLE 1. Acidities of a Number of Compounds and Proton (ΔE_-) and Hydride Ion (ΔE_+) Affinities and the Corresponding Ions Calculated by the CNDO/2 Method

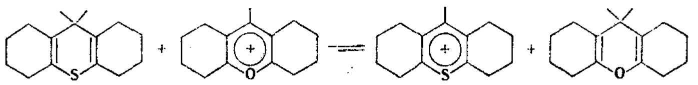
Compound	Symbol	pK_a	ΔE_-, eV	ΔE_+, eV
4H-Thiapyran	Ia	19,5[10]	23,35	31,29
2H-Thiapyran	Ib	20[11]	23,61	31,54
4H-Pyran	IIa	37[10]	24,94	31,33
2H-Pyran	IIb	—	24,89	31,29
2H-Thiapyran 1, 1-dioxide	III	<16[12,13]	22,45	35,16
Cyclopentadiene	IV	15[14]	22,53	36,84
Cycloheptatriene	V	36[15]	24,52	29,89

order III ≈ IV < I < II ≈ V (Table 1). This makes it possible to hope for the possibility of prediction of the relative hydride lability of the hydrogen in the examined compounds from the ΔE_+ values calculated by the standard CNDO/2 method.

At this stage of the theoretical evaluation of the acidities of I-V one can draw certain conclusions. In calculations in the sp basis the ΔE_- values for 4H- and 2H-thiapyrans (25.60 and 25.68 eV, respectively) are higher than for 4H-pyran (24.94 eV); this is not in agreement with the considerably higher acidity of the former. Although the energies of thiapyrans and the thiabenzene anion decrease to small values when the basis is expanded, allowance for the d orbitals of sulfur nevertheless substantially improves the evaluation of the difference in their energies. The vacant 3d orbitals of sulfur should therefore be included in the basis in the theoretical investigation of the reactivities of thiapyrans.

One's attention is drawn to the substantially lower proton affinity of the thiabenzene anion as compared with its oxygen analog. This confirms the previous assumption [16] that the high acidity of thiapyrans is due to the relatively small change in the energy of the heteroring when a proton is detached. For the same reason, the ability of sulfone III to give up a proton is no less than that of cyclopentadiene, the high acidity of which is usually explained by the aromatic character of the cyclopentadienylium anion. On the basis of the data obtained it can be assumed that the acidities of isomeric pyrans are approximately identical.

The hydride lability of hydrogen increases in the order IV < III < II ≈ I < V, since the H^- affinity in the corresponding series of cations decreases (Table 1). In contrast to the first two compounds, thiapyran and pyran are characterized by relatively high H^- lability; this may be the reason for their ability to undergo disproportionation. The results obtained in this research do not contradict the experimental fact that the equilibrium of the ensuing hydride migration is shifted to the right [3]:



At the same time, $\Delta E_+(I) > \Delta E_+(V)$, which is not in agreement with some of the experimental data. Thus the thiapyrylium cation is more stable in alkaline media than the tropylium cation [17]. The equilibrium of the hydride-ion exchange between the thiapyrylium heteroring and the tropylium cation is shifted to favor the formation of thiapyrylium salts [3, 17]. The reduced ability of thiapyrylium compounds to undergo nucleophilic addition as compared with tropylium compounds is evidently associated with the higher degree of solvation of the thiapyrylium heteroring, which is distinguished by a nonuniform charge distribution [18-20].

The increased chemical stability of the thiapyrylium cation was previously explained by the relatively high localization energy [17]. In the π approximation it is assumed that the change in energy (ΔE_+) is due entirely to rearrangement of the π system, whereas the change in the energy of the σ framework is approximatethe same: $\Delta E_{+}^{\sigma}(I) \approx \Delta E_{+}^{\sigma}(V)$. It was found that this assumption is incorrect: the first value substantially exceeds the second.

Thus thiapyran and pyran heterocycles are distinguished by high hydride lability of hydrogen; this is apparently the principal reason for their ability to undergo disproportionation.

The abilities of isomeric thiapyrans and pyrans to give up a hydride ion are approximately identical, cycloheptatriene is a more active H^- donor in low-polarity media. Disproportionation is less characteristic, if it is possible at all, for 2H-thiapyran 1,1-dioxide and cyclopentadiene, which are characterized by relatively low hydride lability of hydrogen.

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RESEARCH ON POLYMEROCYANINES

IV.* SOME NULLOMETHYLIDYNEDIMETHYLIDYNE- AND BIS(NULLOMETHYLIDYNE)DIMEROCYANINE DYES

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A number of bis(nullomethylidyne)- and nullomethylidynedimethylidynedimerocyanines that are rhodanine derivatives with 3,3-dimethylindolenine, benzothiazole, 4,5-diphenylthiazole, and pyridine residues were obtained. The color of the dimerocyanines depends on the basicity of the nitrogen-containing heterocyclic residue and the length and position of the external polymethine chain. A sharp increase in the sensitizing ability is observed on passing from nullomethylidynedimethylidynedimerocyanines to dimethylidynenullomethylidynedimerocyanines.

We have previously investigated the dependence of the color and sensitizing ability of dimerocyanine dyes on the nature and relative basicity of nitrogen-containing heterocyclic residues [2, 3] and electron-donor substituents in the α and α' positions of the polymethine chain [1]. It seemed of interest to ascertain the dependence of the indicated properties on the length and position of the external polymethine chain. With this end in mind we obtained bis(nullomethylidyne)- (I) and nullomethylidynedimethylidynedimerocyanines (II). The cor-

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* See [1] for communication III.

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