

Photochemical Double-Proton-Transfer Reactions in 2,6-Dithiopurine. A Matrix Isolation Study

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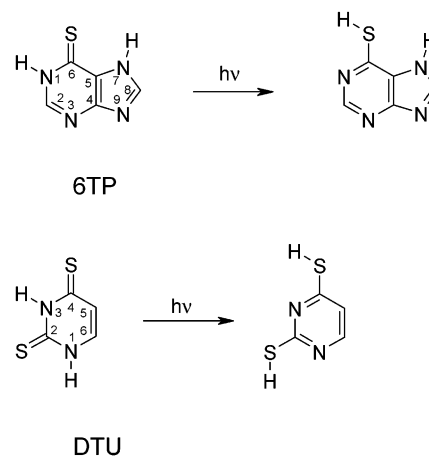
It was found that 2,6-dithiopurine isolated in low-temperature argon and nitrogen matrixes adopts only one tautomeric form: dithione-N7H. The UV ($\lambda > 345$ nm) induced reactions converting this tautomer into dithiol-N3H and dithiol-N7H isomers were observed in Ar and N₂ matrixes. The first of these reactions represents a novel type of photoinduced double-proton transfer, whereas the second is analogous to that previously observed for 2,4-dithiouracil (Lapinski, L.; Nowak, M. J.; Kolos, R.; Kwiatkowski, J. S.; Leszczynski, J. *Spectrochim. Acta A* **1998**, *54*, 685). The assignment of the form initially present in the matrix to the dithione-N7H isomer and of the photoproducts to the dithiol-N3H and dithiol-N7H isomers was based on the good agreement between the experimental IR matrix spectra and the spectra theoretically simulated at DFT(B3LYP)/6-31G(d,p) level.

Introduction

The compound 2,6-dithiopurine has provoked interest and investigation because of its biological activity. This compound has been proposed as a possible chemopreventive agent due to its ability to react with electrophilic toxic metabolites of anticancer drugs.^{1–6}

Several compounds structurally related to 2,6-dithiopurine (DTP) have already been studied by means of matrix isolation infrared spectroscopy. It was established that 2-thiopurine in a low-temperature Ar matrix environment adopts exclusively the thiol-N9H tautomeric form,⁷ while the dominating form of matrix isolated 6-thiopurine (6TP) is the thione-N1H,N7H tautomer.⁸ Upon UV ($\lambda > 325$ nm) irradiation, a photoisomerization process converting the dominant thione tautomer of 6TP into the thiol-N7H form was observed as shown in Scheme 1. Similar UV induced proton-transfer reactions of matrix-isolated species have been previously found for a number of thione heterocyclic compounds, such as 2(1H)-pyridinethione,⁹ 4(3H)-pyrimidinethione, and 3(2H)-pyridazinethione.¹⁰ For 2,4-dithiouracil (DTU), a close pyrimidine analogue of the title compound, the double-proton-transfer reaction leading to 2,4-pyrimidinedithiol form was observed (Scheme 1) in Ar and N₂ matrixes.¹¹ So far, DTU is the only system for which a double-proton-transfer reaction of this type has been found. In all the phototautomeric processes studied hitherto, the proton of the N–H group in the alpha position in the heterocyclic ring (with respect to the thiocarbonyl C=S group) was transferred to the sulfur atom. The mechanism of the photoreaction transforming the thione forms of heterocyclic compounds, mentioned above, into the thiol tautomers is still far from clear. The thione \rightarrow thiol proton-transfer photoreactions, reported for the cases given in refs 7–12, are analogous to the oxo \rightarrow hydroxy phototautomeric reactions observed under low-temperature matrix isolation conditions for some heterocyclic molecules containing carbonyl groups (like 2(1H)-pyridinone).^{13–17} It should be emphasized that all photoreactions of the type specified above are completely

SCHEME 1: Phototautomeric Reactions Observed for 6-Thiopurine (6TP) and 2,4-Dithiouracil (DTU) Isolated in Ar Matrix



different from the known ESIPT (excited-state intramolecular proton transfer) processes.^{18–22} Having an inter- or intramolecular hydrogen bond, and the first excited singlet state of the substrate at higher energy than that of the photoproduct, are both prerequisites for the ESIPT processes. Neither of these conditions is fulfilled in the case of photoinduced proton-transfer reactions oxo \rightarrow hydroxy and thione \rightarrow thiol of the type mentioned above. In the molecules of the compounds analogous to 2(1H)-pyridinethione there are no intramolecular hydrogen bonds and the intermolecular hydrogen bonds are precluded by isolation in inert gas matrixes. Finally, the first excited singlet state of the substrate is placed at lower energy than the first excited singlet state of the product. This is well-known for oxo and hydroxy tautomers, and it has also been established for the thione and thiol forms by studying UV absorption spectra of 6TP and DTU.^{8,11}

The aim of the present work was to study the tautomerism of monomeric DTP and the unusual phototautomeric reactions of this compound, which lead to the production of two different dithiol isomers.

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TABLE 1: Relative Energies (in $\text{kJ}\cdot\text{mol}^{-1}$) of 2,6-Dithiopurine Isomers Calculated at the MP2/6-31G(d,p) Level

isomeric form	dithione N7H (I)	dithione N9H (II)	dithiol N9Ha (IIIa)	dithiol N9Hb (IIIb)	dithiol N7H (VI)
ΔE_{MP2}	0	44.7	49.65	46.99	67.98
$\Delta ZPE_{\text{DFT(B3LYP)}}^a$	0	-2.26	-20.11	-19.6	-21.39
ΔE_{TOT}	0	42.44	29.54	27.39	46.59

^a ZPE: zero-point vibrational energy.

Experimental Section

The 2,6-dithiopurine used in this study was a commercial product (Aldrich). The sample of the compound was electrically heated in a microwave placed in the vacuum chamber of a continuous flow helium cryostat. The vapors of DTP were deposited, together with large excess of an inert gas, on a CsI window cooled to 10 K. The matrix gases (argon and nitrogen of spectral purity) were supplied by Linde AG and Technische Gase, Leipzig. The infrared spectra in the range $4000\text{--}190\text{ cm}^{-1}$ were recorded at a resolution of 0.5 cm^{-1} on a Thermo Nicolet "Nexus" FTIR spectrometer equipped with KBr and "solid substrate" beam splitters, and DTGS detectors. Integral intensities of the IR absorption bands were measured by numerical integration.

Matrixes were irradiated with the light from the high-pressure mercury lamp HBO 200 fitted with a water filter and a cutoff filter (WG 345) transmitting the light with $\lambda > 345\text{ nm}$.

Computational Section

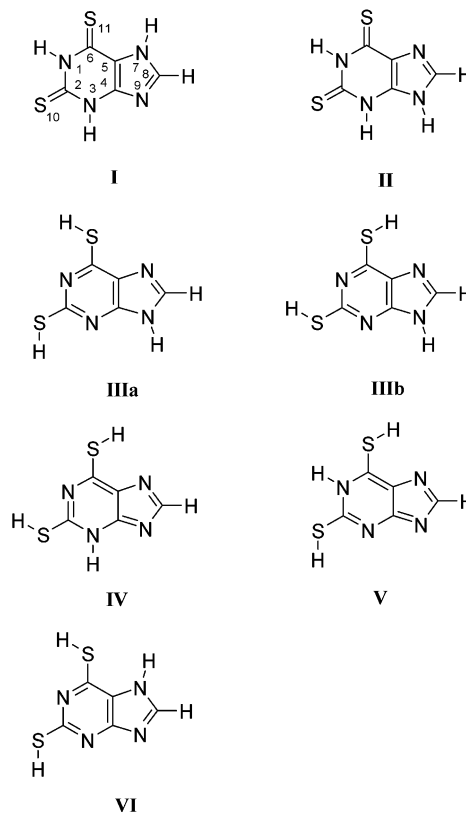
The geometries of the isomers of DTP considered in this work were optimized at the ab initio MP2 level²³ and using density functional theory with Becke's three-parameter exchange functional and gradient-corrected functional of Lee, Yang, and Parr (DFT(B3LYP)).²⁴ All quantum-mechanical calculations were performed using the GAUSSIAN 98 program.²⁵ The standard 6-31G(d,p) basis set was applied in all the cases. The DFT(B3LYP) harmonic vibrational frequencies and IR intensities were calculated for optimized geometries. The predicted vibrational wavenumbers were scaled down by a single factor of 0.98 to correct for systematic shortcomings of the applied methodology (mainly for anharmonicity).

The standard PED analysis²⁶ of the calculated normal modes has been performed. Internal coordinates used in this analysis are given in Table S1 (Supporting Information). The PED matrix elements greater than 10% are listed in Tables S2–4 (Supporting Information).

Results and Discussion

Ground-State Tautomerism. In principle, 2,6-dithiopurine may exist in 20 tautomeric forms. When the rotations of the SH groups in the thiol forms are taken into account, the number of different isomers increases to 44. The forms considered in the present work as candidates for the lowest energy tautomer are shown in Scheme 2. The results of ab initio calculations of the electronic energy performed at the MP2/6-31G(d,p) level are presented in Table 1. According to these results the dithione-N7H tautomer (I) is the most stable, while other isomers are higher in energy by more than $27\text{ kJ}\cdot\text{mol}^{-1}$. For the forms not given in Table 1, the relative energies (with respect to the form I) calculated at DFT(B3LYP)/6-31G(d,p) level were higher than $37\text{ kJ}\cdot\text{mol}^{-1}$. Hence, based on the theoretical predictions, we expect that only one form, namely the form I, should be observed in the inert environment of low-temperature matrixes.

The experimental spectrum of the title compound isolated in an Ar matrix is presented in Figure 1, together with the results of the DFT(B3LYP)/6-31G(d,p) simulation carried out for the

SCHEME 2: Tautomeric Forms of 2,6-Dithiopurine

dithione-N7H tautomer (I). The good agreement between these two spectra strongly supports the conclusion that the compound in the matrix exists exclusively in dithione-N7H tautomeric form (I). The detailed assignment of the absorption bands observed in the spectra of DTP isolated in Ar and N_2 matrixes to the normal modes theoretically predicted for the form I is given in Table S2 (Supporting Information). The spectra simulated for other tautomers differ significantly from the experimental spectrum.

The spectral positions of three bands observed in the high-frequency range (above 3300 cm^{-1}) correspond very well to their counterparts in the spectra of 6TP and DTU measured in the same conditions. The split band due to the stretching N7H vibration (νN7H) was found in the spectrum of DTP at 3462 and 3457 cm^{-1} , while its analogue in the spectrum of 6TP was observed at 3460 cm^{-1} .⁸ Likewise, a nearly perfect match in frequency occurs for the bands due to νN1H (DTP) and due to νN3H (DTU) (note that N1 in a purine base corresponds to N3 in a pyrimidine). In both cases the band appears in Ar matrixes as a split structure with the component frequencies 3404 and 3396 cm^{-1} .¹¹ The molecular fragments surrounding the N7H and N1H groups in DTP are exactly the same as in 6TP and DTU, respectively. The situation is slightly different for the N3H group in DTP. This group is located in the pyrimidine ring in the same position as the N1H group in DTU, but in DTP the proton interacts with the lone pair of the N9 atom from the imidazole ring. This interaction lowers the frequency of the N3H stretching vibration. Therefore, in the spectrum of DTP the

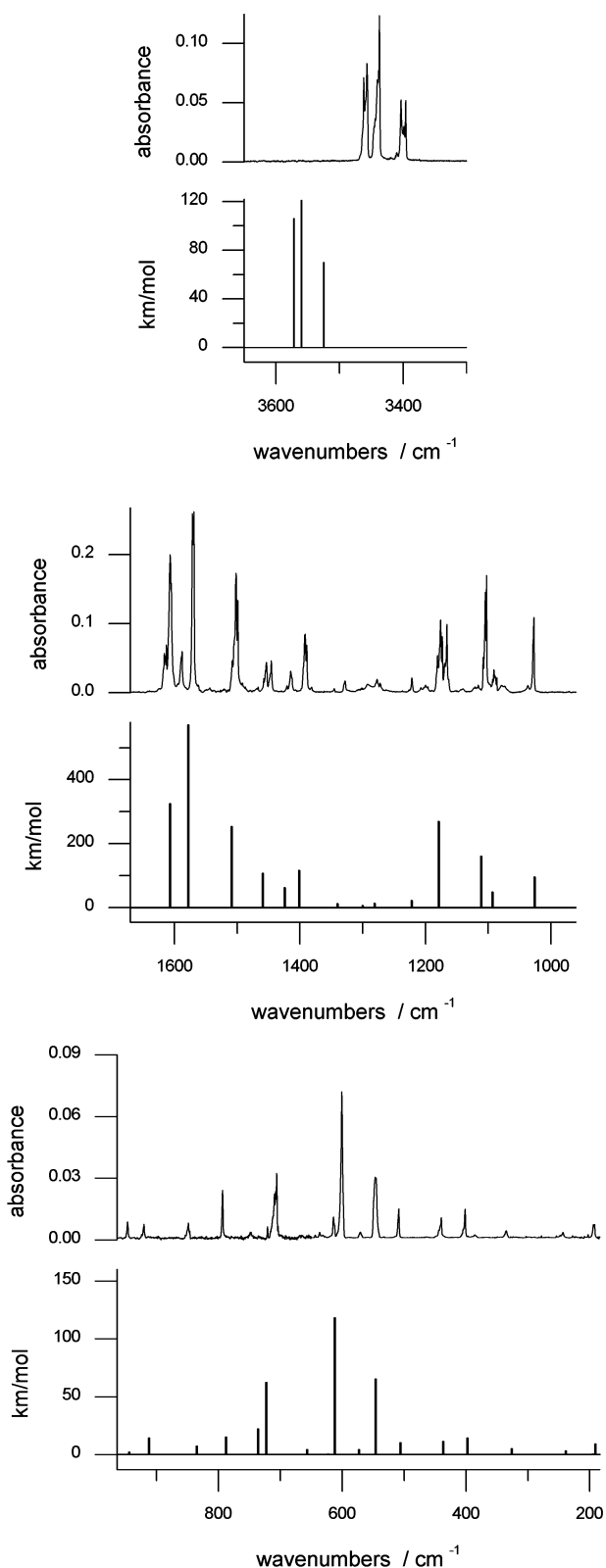


Figure 1. Comparison of the infrared spectrum of DTP isolated in Ar matrix (baseline corrected) with the spectrum theoretically calculated (DFT(B3LYP)/6-31G(d,p)) for the dithione-N7H tautomer (**I**). The theoretical frequencies were scaled by a single factor of 0.98.

corresponding band was found at 3438 cm^{-1} , while in DTU the νN1H band was observed at 3451 cm^{-1} . The spectral positions of the bands in the high-frequency region of the IR spectrum of DTP, together with the general agreement between the experimental spectrum of the monomeric compound and the theoretically predicted spectrum for the dithione-N7H

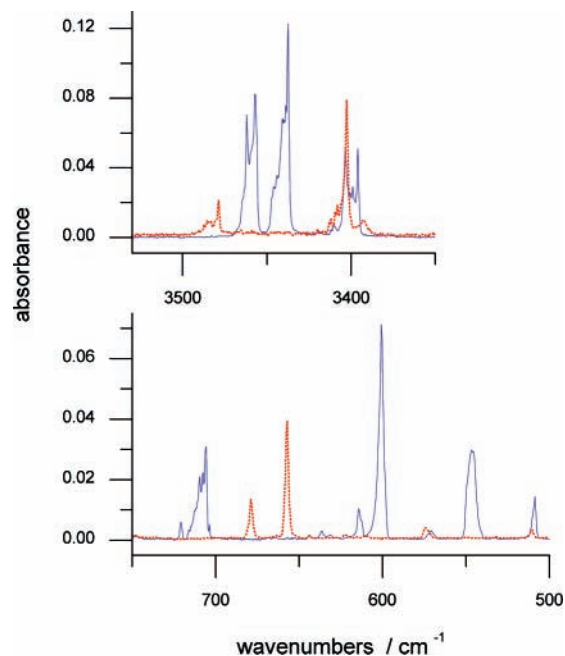


Figure 2. The portions of Ar matrix spectra showing the effect of UV ($\lambda > 345\text{ nm}$) irradiation of the sample: blue solid line, before irradiation; red dotted line, after irradiation.

tautomer (**I**), confirm the presence of this isomer in the matrix. We did not detect in the spectrum any additional bands that could be interpreted as due to another species.

The high stabilization of the dithione-N7H form (**I**) with respect to the dithione-N9H isomer (**II**) can be easily rationalized. In the N9H tautomer, the repulsive interactions between: first, lone electron pairs of the S11 and N7 atoms, and second, hydrogen atoms attached to N3 and N9 nitrogen atoms, destabilize the molecule. On the contrary, in the N7H form, the hydrogens at N3 and N7 atoms interact with the lone pairs of the N9 and S11 atoms, respectively, to lower the total molecular energy.

The tautomeric equilibria in xanthine (the oxo analogue of DTP) should be similar. In the MP2/6-31G(d,p) calculation²⁷ the dioxo-N7H tautomer of this compound was predicted to be the most stable, with the energies of other forms higher by more than $35\text{ kJ}\cdot\text{mol}^{-1}$.

Phototautomerism. Upon UV ($\lambda > 345\text{ nm}$) irradiation of the matrix, the IR bands from the spectrum of the initial form of DTP decrease in intensity and disappear completely after 45 min. A spectrum of new bands due to photoproduct(s) appears instead. The progress of this photoreaction was analyzed while the time of irradiation was gradually increased from 1 min up to 45 min. No bands due to any intermediate photoproduct were observed at any stage of the photoreaction. The portions of the spectra obtained before and after 45 min of irradiation are shown in Figure 2.

A significant feature of the new spectrum (see Figure 3) is the appearance of the absorptions at 2617 , 2598 , and 2552 cm^{-1} indicating the presence of the thiol form(s) of the compound. A frequency near 2600 cm^{-1} and a weak IR intensity characterizes bands due to SH stretching vibration. By analogy with the photoreaction previously observed for DTU (see Scheme 1) one could expect that the photoreaction in DTP is a double-proton transfer leading to the dithiol-N7H tautomer (**VI**) (as shown in Scheme 3). In the spectrum of such tautomer only one band (due to νN7H vibration) should appear in the frequency range above 3300 cm^{-1} . In the thiol-N7H form of 6TP, the νN7H band was observed at 3485 and 3481 cm^{-1}

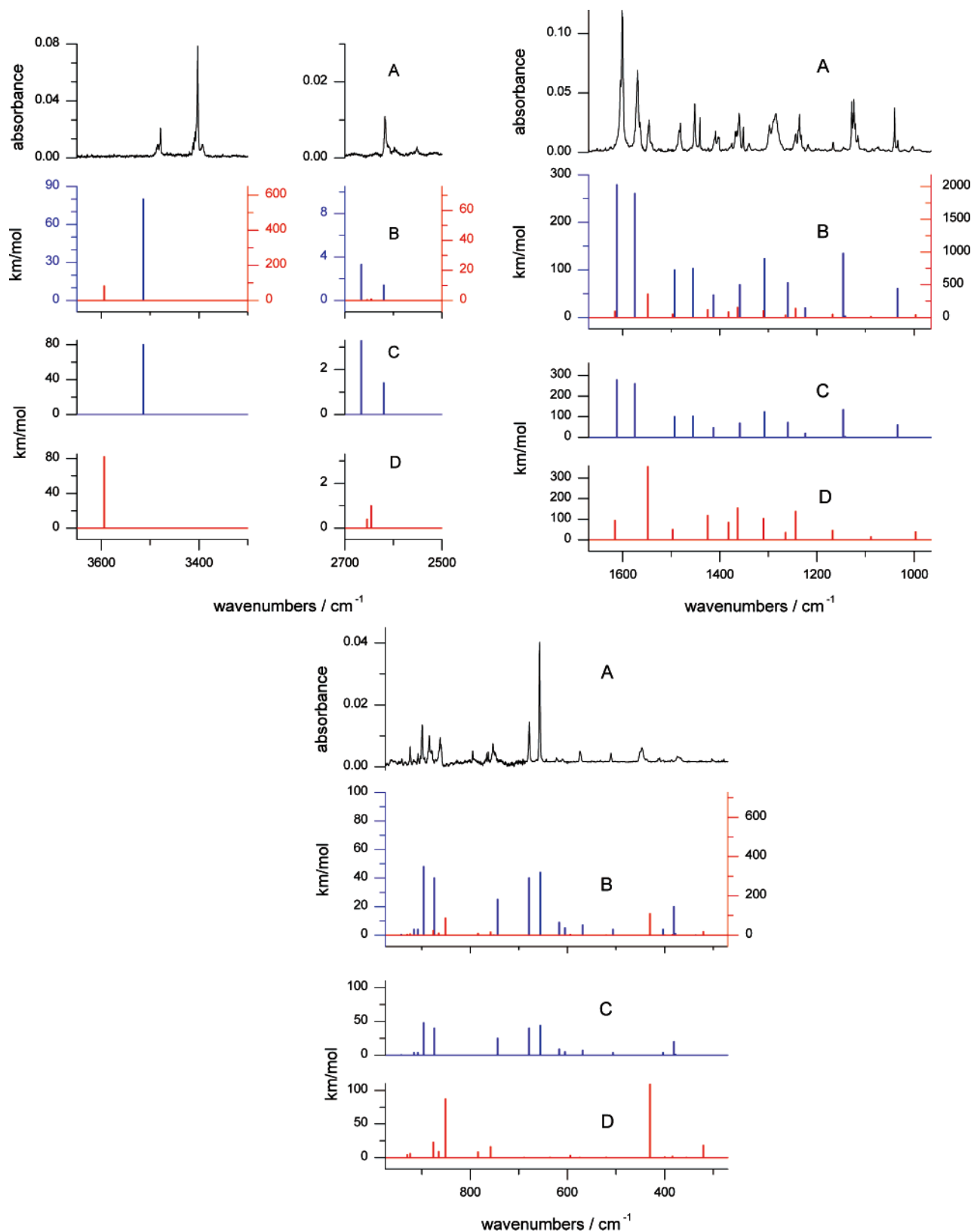
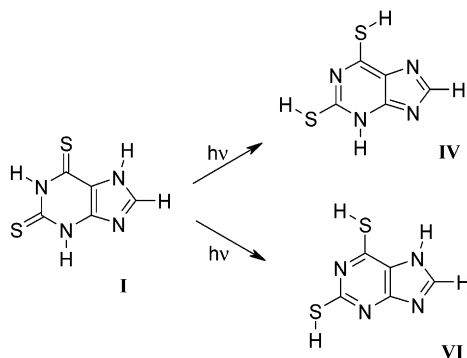


Figure 3. Comparison of the infrared spectrum of the photoproduct(s) created upon UV irradiation of DTP isolated in Ar matrix (baseline corrected) (A) with the spectra theoretically calculated (DFT(B3LYP)/6-31G(d,p)) for the dithiol-N3H (IV) (blue) and dithiol-N7H (VI) (red) tautomers. The superposition of both theoretical spectra is shown in B. To get a match to the observed spectrum, the absolute intensity scale corresponding to the spectrum of form VI was expanded 7.3 times more than the scale corresponding to the form IV. The calculated spectra of tautomers IV and VI are shown separately in C and D, respectively. The theoretical frequencies were scaled by a single factor of 0.98.

(splitting), so an analogous band should appear in the spectrum of photoproducted dithiol-N7H form (VI) of DTP at similar frequency. Indeed, a split band at 3484 and 3479 cm^{-1} has been found in the spectrum of DTP after UV irradiation. But apart

from this band, another, stronger band peaks in the spectrum of photoproduct(s) at 3403 cm^{-1} (see Figures 2 and 3). This led to the assumption that the dithiol-N7H tautomer (VI) is a minor photoproduct and that another major photoproduct has

SCHEME 3: Phototautomeric Reactions Observed for 2,6-Dithiopurine Isolated in Ar Matrix


been created upon electronic excitation of the matrix-isolated DTP.

To identify the main photoproduct, infrared spectra of some of the most probable structures have been theoretically calculated and compared with the experimental spectrum obtained after UV irradiation. The agreement between experiment and theory was generally poor: an example is given in Figure S1 (Supporting Information), where the comparison between the experimental spectrum and the spectrum calculated for the dithiol-N1H form (V) is presented. Only the theoretically predicted spectrum of dithiol-N3H structure (IV) reproduces well the stronger absorption bands in the experimental spectrum, while the second set of remaining weaker absorptions coincides with the predicted spectrum of dithiol-N7H (VI) form. Hence, we concluded that dithiol-N3H structure (IV) is the main photoproduct whereas the initially expected dithiol-N7H form (VI) is a minor product.

Figure 3 shows the IR spectrum of DTP after irradiation alongside a superposition of the simulated spectra of dithiol-N7H (VI) and dithiol-N3H (IV) tautomers. The overall agreement between these spectral patterns is apparent. Moreover, the following features should be pointed out: (i) The two ν NH bands in the experimental spectrum are separated by 76 cm^{-1} , while the difference in frequencies of the ν NH bands, calculated for dithiol-N7H (VI) and dithiol-N3H (IV) forms, is very similar: 80 cm^{-1} . [Due to the cancellation of systematic errors, the relative frequencies of the modes of the same type (ν NH) should be properly predicted by theoretical calculations.] (ii) The most intense band in the spectrum of the minor, dithiol-N7H form (VI) is clearly seen at 1546 cm^{-1} ; fortunately, it is not obscured by the bands due to the main photoproduct. (iii) The pattern of the three bands at 899 , 879 and 862 cm^{-1} is well-reproduced in the theoretical spectra by two bands from the spectrum of the dithiol-N3H form (IV) (896 and 874 cm^{-1}) and the band of the dithiol-N7H form (VI) (851 cm^{-1}). (iv) The absorption band observed in the spectrum of the photoproduct at 447 cm^{-1} has been interpreted as due to wagging vibration γ N7H of the dithiol-N7H form (VI); the analogous γ N7H band was observed in the spectrum of the thiol-N7H form of 6TP at a similar frequency: 456 cm^{-1} . All these observations strongly support the conclusion about the identity of two photoproducts (as they are presented in Scheme 3).

The majority of the experimental bands from the spectrum of the photoproducts was assigned to the normal modes of the respective tautomeric forms IV and VI. This assignment was based on similarities between experimental and theoretically predicted band frequencies and relative intensities (available in Supporting Information in Table S5). The frequencies, absolute intensities and PED's of forms IV and VI obtained theoretically

at DFT(B3LYP)/6-31G(d,p) level are listed in Tables S3 and S4, respectively.

The photoreaction converting the initial dithione-N7H form (I) of DTP into the dithiol-N7H tautomer (VI) is a direct analogue of the reaction previously observed for DTU. It represents the second reported example of such double-proton-transfer photoreaction. The reaction leading to the dithiol-N3H isomer (IV) involves photoinduced proton transfer from the nitrogen atom in position other than alpha (with respect to C=S group). Such photoreactions have not been observed so far.

In all known cases of photoinduced single- or double-proton-transfer reactions (of the type in question) the distance between the NH proton and the alpha sulfur atom was about 2.79 \AA . The calculated distance between the N7H proton and the S11 sulfur in the dithione-N7H tautomer (I) of DTP is greater, namely, 3.1509 \AA (MP2), 3.1776 \AA (DFT). So, considering the distances only, the dithiol-N7H form (VI) should be expected as the main photoproduct. The experimental findings do not support this hypothesis. The dominance of the dithiol-N3H phototautomer (IV) may result from the fact that the angle C6-S11-H(N7) of 65.6° is more favorable than the angle C6-S11-H(N1) of 47.1° . The wider angle can promote the interaction of the N7H proton with the lone pair of the S11 atom. The angle of 65.6° is closer to the typical value of C-S-H angle ($93-94^\circ$) in thiol forms. The stabilizing interaction of N3H proton with the lone pair of N9 nitrogen atom can also compete (to some degree) with the attraction of this proton to S10 sulfur atom and contribute to the shift of photoproduct distribution in favor of the dithiol-N3H tautomer (IV).

Photoreactions transforming the thione forms of simple thioamides (thiourea and thioacetamide) to the corresponding thiol tautomers were recently discovered in our laboratory. The mechanism of the phototautomeric reactions observed in these thioamides and in heterocyclic compounds, such as DTP, is most probably the same. Elucidation of this mechanism will be the aim of our further studies of phototautomerism in small thioamides.

Supporting Information Available: Table S1 provides internal coordinates used in the normal-mode analysis for the tautomers of 2,6-dithiopurine. Table S2 provides the spectra of 2,6-dithiopurine isolated in Ar and N₂ matrixes assigned to the theoretically calculated spectrum of the form I. The theoretically calculated spectra of forms IV and VI are presented in Tables S3 and S4. In Table S5 the experimental absorption bands of 2,6-dithiopurine after irradiation are assigned to the theoretically predicted normal modes for the forms IV and VI. The comparison of the infrared spectrum of the photoproducts created upon UV irradiation of DTP isolated in Ar matrix with the spectra theoretically calculated for the forms IV and V is presented in Figure S1. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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