Spectrochimica Acta Part A 54 (1998) 685–693

SPECTROCHIMICA
ACTA
PART A

Spectroscopic identification of 2,4-pyrimidinedithiol; an experimental matrix isolation and ab initio Hartree–Fock and density functional theory study

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Received 28 October 1997; received in revised form 28 October 1997; accepted 18 November 1997

Abstract

2,4-Pyrimidinedithiol (the dithiol form of 2,4-dithiouracil) was generated by UV ($\lambda > 335$ nm) irradiation of the dithione form of 2,4-dithiouracil isolated in low-temperature argon or nitrogen matrices. The IR and UV spectra of the photoproduct are reported. The dithiol form of 2,4-dithiouracil was identified by comparison of the experimental spectrum with the spectrum theoretically predicted for this form at the HF/6-31 (d,p) and DFT(B-3LYP)/6-31 (d,p) levels. This comparison resulted also in assignment of the bands observed in the IR spectrum of 2,4-pyrimidinedithiol to the theoretically predicted normal modes. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: 2,4-Dihiouracil; 2,4-Pyrimidinedithiol; Photochemistry; Proton transfer; Matrix isolation; Infrared spectra; UV spectra; Ab initio; Density functional theory

1. Introduction

The chemical and physical properties of nucleic acid bases and their derivatives are of continuous interest. Among numerous experimental methods the matrix-isolation offers the possibility of investigation of the bases in conditions in which the intermolecular interactions are minimized. Since the gas phase tautomeric equilibria are frozen during deposition of the matrix, this technique has proven to be very useful for the studies of tautomerism of the nucleic acid bases [1–5]. Along with the 'normal' forms of cytosine and guanine, the 'rare' tautomers of these compounds were found in rare gas low-temperature matrices [2,3,5,6]. Adenine, uracil and thymine were observed in matrices exclusively in their 'normal' tautomeric forms [1,7,8]. An inert, low-temperature environment can also stabilize the 'rare' tau-

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PII S1386-1425(97)00278-3

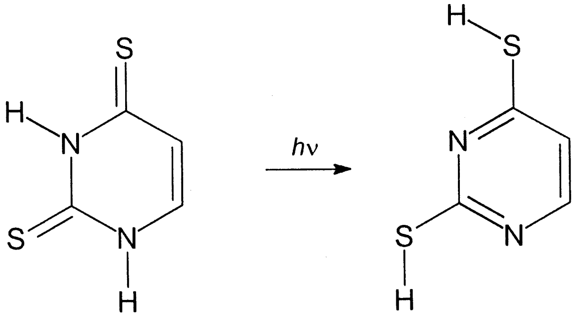
tomeric forms produced photochemically in the matrix. A UV induced proton transfer from the nitrogen atom in the heterocyclic ring to the exocyclic oxygen, changing the oxo form into the hydroxy tautomer, was discovered in this laboratory for 4(3H)-pyrimidinone isolated in low-temperature inert gas matrices [9]. Next, similar photoreactions were found for matrix-isolated 2(1H)-pyridinone [10], 3(2H)-pyridazinone [11] and cytosine [2]. Similar photoreactions were subsequently observed for a number of thione compounds: 2(1H)-pyridinethione [12], 3(2H)-pyridazinethione [13], 4(3H)-pyrimidinethione [13] and 2(1H)-quinolinethione [14]. The phototautomeric reactions, listed above, are entirely different from those known as ESIPT (excited state intramolecular proton transfer) processes [15,16]. ESIPT always occurs in systems having proton donor and acceptor linked by hydrogen bond. Proton transfer undergoes from excited singlet state which is placed higher in energy scale than the respective excited singlet state of the product (tautomer). The obtained form (tautomer) is not stable in the ground state and a back proton transfer ends ESIPT process. None of this features concerns oxo → hydroxy or thione → thiol phototautomeric reactions mentioned in Refs. [2,9–14]. ln these cases no intramolecular hydrogen bonds are present. The possibility of existence of intermolecular hydrogen bonds is excluded since the phototautomeric reactions were observed only for monomeric, isolated in low-temperature matrices, molecules. The mechanism of proton transfer is different than that in the case of ESIPT because the energy of the first excited singlet state of produced tautomer is higher than the energy of the first excited singlet state of the substrate. In low-temperature matrices the produced enol (or thiol) tautomers are stable and were detected in their ground states.

Up to now the 'rare' hydroxy forms of uracil (or thymine) and the corresponding 'rare' hydroxy-thiol forms of thiouracils have never been obtained by thermal (in the vapour state) or photochemical population method. The dithiol form of 2 4-dithiouracil is the first case for which the 'rare' uracil tautomer of them was formed [17]. This tautomeric form was obtained from the normal dithione form in a reaction presented in Scheme 1. This is the first example of a photoinduced double proton transfer of the type quoted above.

The nucleic acid bases with a sulfur atom instead of oxygen in uracil have been a subject of considerable interest since they were detected in natural tRNAs [18]. Thiouracil's derivatives attract attention not only because of their unclear role in nucleic acid structures but also because of exhibited pharmacological activities. For example a series of 1-amino-5-substituted 4-thio or 2,4-dithio uracil analogues were assayed for anticonflict and anestethic activity in rats or mice [19]. 2,4-Dithiouracil was found to be a melanoma-seeking agent owing to its specific incorporation in nascent melanin [20].

The UV absorption spectra of 2,4-dithiouracil in water solutions and IR spectra of the compound in DMSO solutions were reported by Psoda and Shugar [21]. Ultraviolet absorption, circular dichroism and magnetic circular dichroism spectra of 2,4-dithiouracil in aqueous and acetonitrile solutions were measured by Igarashi-Yamamoto et al. [22]. The UV absorption and phosphorescence spectra of this compound in EPA glass were collected by Pownall et al. [23]. Phosphorescence and ODMR spectra of 2,4-dithiouracil were reported by Taherian and Maki [24]. Vibrational spectra of 2,4-dithiouracil in water neutral solutions were studied by means of resonance Raman spectroscopy by Ghomi et al. [25].

The IR spectra of 2,4-dithiouracil isolated in low-temperature matrices were previously re-



Scheme 1.

ported [26–28]. From the analysis of those spectra it was clear that the compound adopts exclusively the dithione form while isolated in low-temperature matrices.

Relative energies of different 2,4-dithiouracil tautomers were theoretically predicted by Leszczyński and Lammertsma at the MP2/6-31G*//3-21G(*) level with inclusion of zero-point energy corrections [29]. The dithione tautomer was found to be the most stable structure and the difference with the dithiol tautomer was predicted to be as high as 28 kJ mol^{-1}.

2. Experimental section

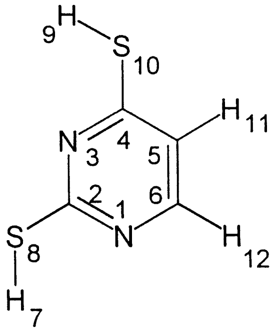
The 2,4-dithiouracil used in this study was kindly made available to us by Professor D. Shugar (Warsaw). The compound was heated in a microoven placed in the vacuum chamber of the cryostat. The vapors of 2,4-dithiouracil were deposited, together with large excess of argon, on a CsI (or sapphire for UV spectroscopy) window cooled to 10 K. The matrix gases argon and nitrogen of the spectral purity were supplied by Linde AG, and Technische Gase (Berlin, Germany), respectively. The infrared spectra were recorded with a Perkin-Elmer 580B grating spectrometer or with FTIR spectrometer Nicolet 170 SX. Integral intensities of the IR absorption bands were measured by numerical integration.

UV absorption spectra were taken using a 480 mm focal length monochromator (Digikroem 480), deuterium lamp and Philips XP2020 photomultiplier. The signal was registered in the single photon counting mode.

Matrices were irradiated with the light from the high pressure mercury lamp HBO 200 fitted with a water filter and a cut-off filter (WG 335) transmitting the light with $\lambda > 335$ nm. The time of irradiation was 1 h.

3. Computational details

The geometry of planar dithiol form of 2,4-dithiouracil (Scheme 2) was optimized at the ab initio Hartree–Fock (HF) [30] level and using the density functional theory with the Becke's three-parameter exchange functional and gradient-corrected functional of Lee, Yang and Parr (DFT(B3-LYP)) [31]. In the calculations a split-valence basis set augmented by a set of six d functions on heavy atoms and three p functions on hydrogens (the 6-31G(d,p) basis set) was used [30]. The HF and DFT(B3-LYP) approaches were used to predict the harmonic vibrational wavenumbers and absolute intensities at the corresponding optimized geometries of the molecule. All quantum-mechanical calculations were performed using the GAUSSIAN 92/DFT program [32]. Note that the DFT-optimization was carried out with the options Opt = Tight and Int = FineGrid, and the vibrational calculations were done with the option Int = FineGrid.



Scheme 2. Atom numbering for: 2,4-pyrimidinedithiol.

The predicted vibrational wavenumbers were scaled down by a single factor of 0.98 or 0.9 in the case of DFT(B3-LYP) or HF calculations, respectively (to correct for systematic shortcomings of the quantum-mechanical methodology, mainly to correct for anharmonicity). The theoretically calculated force constant matrices in Cartesian coordinates were transformed to molecular internal coordinates in order to enable standard potential energy distribution (PED) analysis [33] of the normal modes. The internal coordinate set used in the PED calculation is the same as that used in Ref. [25], except for the coordinates associated with the SH group (the SH stretching (νSH), in-plane bending (βSH) and out-of-plane torsional (τSH) modes). These coordinates were defined in a standard way, the same as that

Table 1

Experimental wavenumbers ($\tilde{\nu}$), integral intensities (I) and theoretically calculated wavenumbers, absolute intensities (A^{th}) and potential energy distribution (PED) of the absorption bands of 2,4-pyrimidinedithiol

Experimental				Calculated			Calculated		
Ar matrix		N_2 matrix		DFT/6-31G(d,p)			HF/6-31G(d,p)		
$\tilde{\nu}$ cm^{-1}	I rel	$\tilde{\nu}$ cm^{-1}	I rel.	$\tilde{\nu}^{\dagger}$ cm^{-1}	A^{th} km mol^{-1}	PED (%)	$\tilde{\nu}^{\dagger}$ cm^{-1}	A^{th} km mol^{-1}	PED (%)
				3163	1	ν C5H (97)	3061	2	ν C5H (95)
				3112	20	ν C6H (97)	3023	23	ν C6H (95)
2617 2614 2610 2603 2599	15	2615 2602	24	2657	0.4	ν S8H (100)	2632	0.4	ν S8H (100)
				2647	0.1	ν S10H (100)	2631	0.8	ν S10H (100)
1627	10	1628	14						
1586	3	1599	3						
1557 1554 1545 1542	416	1556 1543	444	1574	337	ν C5C6 (33), β C6H (17), ν C6N1 (15), ν N3C4 (13), ν C2N3 (10)	1600	454	ν C5C6 (30), ν C6N1 (15), β C6H (15), ν C2N3 (14), ν CN3C4 (13)
1530 1526 1521	57	1529 1524	69	1551	168	ν C4C5 (34), ν N1C2 (16), ν C6N1 (12), ν C5H (10)	1577	268	ν C4C5 (27), ν N1C2 (24), ν N3C4 (13), ν C6N1 (12)
1450	4	1448	6						
1421 1417 1413 1399	164	1423 1415	146	1422	132	β C6H (29), β C5H (26), ν N3C4 (23), ν N1C2 (15)	1438	130	β C5H (31), β C6H (23), ν N3C4 (20), ν N1C2 (12)
1335	202	1335	202	1347	197	ν C2N3 (42), β C6H (20), β R1 (13)	1354	276	ν C2N3 (41), β C6H (21), ν C6N1 (11)
1265 1260	6	1271	7	1239	30	ν N1C2 (32), ν N3C4 (24), ν C6N1 (13)			
							1230	78	β C6H (23), β R1 (22), ν N1C2 (21), ν C2S (13)
1224 1222	99	1233 1224 1216	112	1220	103	ν C6N1 (20), β R1 (19), β C6H (18), ν C2N3 (13), ν C2S (11)			
							1176	48	ν C4C5 (18), β R1 (16), ν C4S (14), ν C5C6 (13), ν N3C4 (12), β C6H (11)

Table 1 (*Continued*)

Experimental				Calculated			Calculated		
Ar matrix		N_2 matrix		DFT/6-31G(d,p)			HF/6-31G(d,p)		
$\tilde{\nu}$ cm^{-1}	I rel	$\tilde{\nu}$ cm^{-1}	I rel.	$\tilde{\nu}^{\dagger}$ cm^{-1}	A^{th} km mol^{-1}	PED (%)	$\tilde{\nu}^{\dagger}$ cm^{-1}	A^{th} km mol^{-1}	PED (%)
1185		1187							
1181		1185	24						
1177	73	1180	38	1173	57	ν C4C5 (23), β R1 (20), ν C4S (14), ν C5C6 (12)			
							1116	3	ν C6N1 (33), β C5H (26), ν N3C4 (18)
1101	3	1101	3	1103	5	β C5H (48), ν C5C6 (25), ν C6N1 (10)			
							1076	26	ν C5C6 (38), β C5H (17), ν C4C5 (11)
				977	0.1	γ C6H (93), γ C5H (20)	1017	0.1	γ C6H (95), γ C5H (17)
				975	0.4	β R1 (43), ν N1C2 (12), ν C2N3 (11), ν N3C4 (11), ν C6N1 (10)	982	3	β R1 (42), ν C6N1 (12), ν C2N3 (12), ν N1C2 (10)
		961	3						
				914	1	β S8H (59), β S10H (26)	931	3	β S8H (75)
912	4	909	3						
900	5	886	5						
871	6								
				894	21	β S10H (62), β S8H (29)	912	25	β S10H (78), β S8H (10)
				813	17	γ C5H (87), γ C6H (13)	826	27	γ C5H (89), γ C6H (11)
824		826							
815	104	817	78						
806		809		810	81	β R2 (23), β R3 (20), ν C2S (19), ν C4S (19)	814	60	β R2 (21), ν C2S (20), β R3 (20), ν C4S (19)
771	4	772	3	771	7	τ R1 (82), γ C2S (19)	787	19	τ R1 (78), γ C2S (21)
689	22	689	22	683	20	β R3 (44), β R2 (24), ν C4C5 (10), ν C4S (10)	679	19	β R3 (43), β R2 (24), ν C4C5 (11), ν C4S (10)
				606	0.7	γ C4S (45), γ C2S (37), τ R2 (16)	616	1	γ C4S (44), γ C2S (35), τ R2 (17)

Table 1 (*Continued*)

Experimental				Calculated			Calculated		
Ar matrix		N_2 matrix		DFT/6-31G(d,p)			HF/6-31G(d,p)		
$\tilde{\nu}$ cm^{-1}	*I* rel	$\tilde{\nu}$ cm^{-1}	*I* rel.	$\tilde{\nu}^{\dagger}$ cm^{-1}	A^{th} km mol^{-1}	PED (%)	$\tilde{\nu}^{\dagger}$ cm^{-1}	A^{th} km mol^{-1}	PED (%)
				434	1	ν C2S (42), β R2 (26), β R3 (18)	434	1	ν C2S (41), β R2 (27), β R3 (18)
				429	0.6	τ R3 (62), γ C2S (14), τ R2 (11)	436	2	τ R3 (63), γ C2S (12), τ R2 (12), τ R1 (10)
				402	0.1	ν C4S (41), γ C2S (17), β R2 (16)	402	0.5	ν C4S (39), ν C2S (17), β R2 (16)
347	6	346	6	343	6	β C2S (45), β C4S (44)	343	7	β C2S (45), β C4S (43)
314	13			317	13	τ S8H (94)	305	20	τ S8H (99)
				294	36	τ S10H (94)	258	37	τ S10H (99)
				184	1	β C2S (44), β C4S (44)	182	1	β C4S (45), β C2S (43)
				165	0.2	τ R3 (38), γ C4S (34), τ R1 (15), γ C2S (12)	170	0.3	τ R2 (40), τ R3 (31), γ C4S (27)
				155	2	τ R2 (79), γ C2S (18)	164	2	τ R2 (38), γ C2S (33), τ R1 (13)

[a] Theoretical positions of absorption bands were scaled: for DFT calculations by a factor 0.98 and for HF by 0.9. PED's lower than 10% are not included.

Abbreviations: *I*, internal absorbances of IR bands normalized in such a way that the observed intensity sum of all assigned bands is equal to the calculated (at the DFT(B3-LYP)/6-31G(d,p) level) intensity sum of the corresponding bands. A^{th}, calculated intensities; rel, relative; ν, stretching; β, bending in-plane; τ, wagging; γ, bending out-of-plane.

applied in Refs. [12,14]. The contributions to the PED values of less than 10% (Table 1) are not included.

4. Results and discussion

The survey IR spectra of 2,4-dithiouracil isolated in the Ar matrix are presented in Fig. 1A. These spectra are identical with those previously reported [26].

The spectra resulting after 1 h of UV ($\lambda > 335$ nm) irradiation of the matrix are shown in Fig. 1B. The remarkable feature of the spectra of the photoproduct is the absence of any absorptions in the high frequency region, in which for the spectra of the dithione form the bands due to NH stretching vibrations were present. At 2610 and 2603 cm^{-1} (Fig. 1B and 2) a weak absorption band, split into several components, due to SH stretching vibrations was observed in the spectrum collected after UV irradiation of the matrix. In this spectral region no bands due to other vibrations

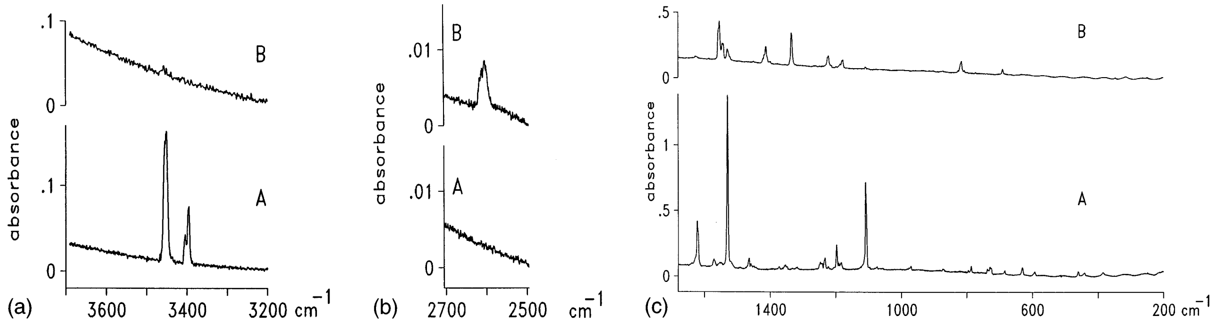


Fig. 1. The infrared spectra of 2,4-dithiouracil isolated in Ar matrix; (A) before irradiation, (B) after UV ($\lambda > 335$ nm) irradiation of the matrix.

are expected, and that is why the assignment of the observed spectral feature to νSH vibrations seems reliable. The other vibrations of SH groups give rise to the bands of even lower intensity. The bands due to torsional vibration of SH groups expected near 300 cm^{-1} could only be traced in an Ar matrix. For other thiol heterocyclic compounds the usually weak τSH bands were observed only in very few cases [12–14,34–36]. Also in thiol compounds the bands due to SH bending in plane vibration are very weak and were rarely detected in IR matrix spectra [12–14,34–36].

Comparison of the experimental spectrum of the photoproduct with the spectrum theoretically predicted (at the DFT(B-3LYP)/6-31G(d,p) and HF/6-31G(d,p) levels) for the 2,4-pyrimidinedithiol structure is shown in Figs. 2 and 3. A good overall agreement between these spectra is clearly seen. The most intense bands in the experimental spectrum (1530, 1413, 1335, 1222, 1177 and 815 cm^{-1}) have their well predicted counterparts in the spectra theoretically calculated at both DFT and HF levels. The lack of any high or medium intensity bands in the ranges 1100–800 cm^{-1} and 600–300 cm^{-1} is a further similarity between experimental and theoretical spectra.

The frequencies and intensities of the bands observed in the experimental spectrum of the photoproduct are collected in Table 1 together with those of the IR bands theoretically predicted for the 2,4-pyrimidinedithiol structure. The proposed assignment is also shown in this table.

The UV absorption spectra of 2,4-dithiouracil isolated in Ar matrix are shown in Fig. 4. These spectra are quite similar to those of the compound in the EPA glass [23], water solution [21,22,25] and to the spectra of 2,4-dithiouracil in the gas phase [37]. The maximum of the strong band due to the ππ* transition is placed at 276 nm. At longer wavelengths a weaker band is observed in which the vibrational structure may be seen. The

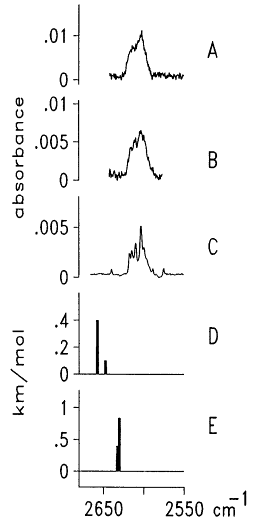


Fig. 2. The 2700–2550 cm^{-1} region (where the bands due to νSH vibration are expected) of the infrared spectrum of 2,4-pyrimidinedithiol: (A) isolated in N_2 matrix; (B) isolated in Ar matrix; (C) isolated in Ar matrix (high resolution FTIR measurement); (D) the bands due to νSH vibrations theoretically calculated at the DFT(B3-LYP)/6-31G(d,p) level; (E) calculated at the HF/6-31G(d,p) level.

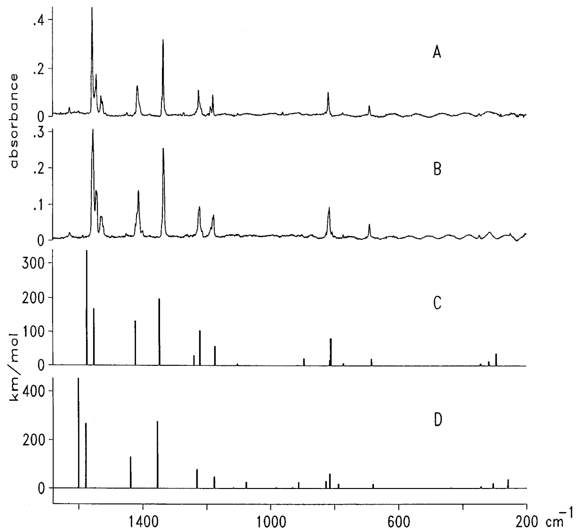


Fig. 3. (A) The infrared spectrum of 2,4-pyrimidinedithiol isolated in N_2 matrix; (B) isolated in Ar matrix; (C) IR spectrum of 2,4-pyrimidinedithiol theoretically calculated at the DFT(B3-LYP)/6-31G(d,p) level; (D) calculated at the HF/6-31G(d,p) level.

long wavelength end of this band is at 379 nm. After UV irradiation of the matrix, with the light ($\lambda > 335$ nm) from the high pressure mercury lamp, the UV absorption spectra change considerably. In comparison with the initial spectrum the bands in the spectrum recorded after UV irradiation are observed (Fig. 4) at shorter wavelengths (227, 287 and 299 nm for the two maxima and a long wavelength end, respectively). The studies [38] of the UV spectra of thio-derivatives of pyridine and pyrimidine in the gas phase indicate that the long wavelength (~ 350 nm) band is characteristic for the thione tautomer, while no absorptions are present at these wavelengths in the spectra of the thiol tautomer. Hence, the effect observed in the present work is in agreement with what one can expect assuming a dithione → dithiol photoreaction.

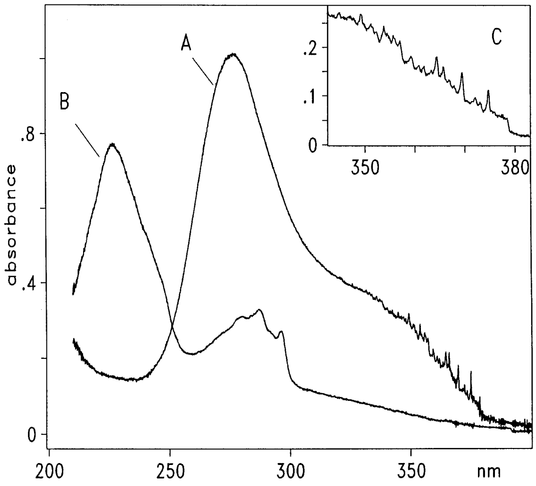


Fig. 4. The UV absorption spectra of 2,4-dithiouracil isolated in Ar matrix; (A) before irradiation, (B) after UV ($\lambda > 335$ nm) irradiation of the matrix, (C) expanded fragment of the spectrum before irradiation recorded using Xe lamp as a light source.

5. Conclusion

The following reasons allow for a conclusion that the photoproduct of the UV irradiation of 2,4-dithiouracil is a dithiol form of the compound:

- appearance of the bands due to SH stretching in the spectrum after irradiation;
- the overall agreement between the observed IR spectrum of the photoproduct and the theoretical predictions;
- similar thione → thiol photoreactions were previously observed though for single proton transfer only;
- the UV spectra of the photoproduct are in agreement with the spectra of other thiol heterocyclic compounds.

Acknowledgements

This study has been supported at Warsaw by the European Union grant No. CIPA-CT 93-0108; at Torun by the internal grant of the Institute of Physics, and at Jackson by the NIH grant # S06-GM08047 and by the contract (DAAL 03-89-0038) between the Army Research Office and the University of Minnesota for the Army High Performance Computing Research Center under the auspices of the Department of the Army Research Laboratory cooperative agreement number DAAH04-95-2-0003/contract number

DAAH04-95-C-008, the content of which does not necessarily reflect the position or the policy of the government, and no official endorsement should be inferred.

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