

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231639931>

# Double-Proton-Transfer Processes in Dithiooxamide: UV-Induced Dithione → Dithiol Reaction and Ground-State Dithiol → Dithione Tunneling

ARTICLE in THE JOURNAL OF PHYSICAL CHEMISTRY A · MAY 2004

Impact Factor: 2.69 · DOI: 10.1021/jp049263w

CITATIONS

11

READS

37

6 AUTHORS, INCLUDING:



[Leszek Lapinski](#)

Polish Academy of Sciences

124 PUBLICATIONS 2,589 CITATIONS

[SEE PROFILE](#)



[Müjgan Yaman Özkütük](#)

Eskisehir Osmangazi University

8 PUBLICATIONS 45 CITATIONS

[SEE PROFILE](#)



[Rui Fausto](#)

University of Coimbra

330 PUBLICATIONS 4,496 CITATIONS

[SEE PROFILE](#)



[Maciej J Nowak](#)

Institute of Physics of the Polish Academy of ...

107 PUBLICATIONS 2,792 CITATIONS

[SEE PROFILE](#)

# Double-Proton-Transfer Processes in Dithiooxamide: UV-Induced Dithione $\rightarrow$ Dithiol Reaction and Ground-State Dithiol $\rightarrow$ Dithione Tunneling

Leszek Lapinski,<sup>†,‡</sup> Hanna Rostkowska,<sup>†</sup> Artem Khvorostov,<sup>†</sup> Mijgan Yaman,<sup>‡</sup> Rui Fausto,<sup>‡</sup> and Maciej J. Nowak<sup>\*,†</sup>

*Institute of Physics, Polish Academy of Sciences, Al. Lotnikow 32/46, 02-668 Warsaw, Poland, and Department of Chemistry, University of Coimbra, P-3004-535 Coimbra, Portugal*

*Received: February 18, 2004; In Final Form: April 20, 2004*

Dithiooxamide [rubeanic acid,  $\text{NH}_2\text{C}(=\text{S})\text{C}(=\text{S})\text{NH}_2$ ] monomers were studied by FTIR spectroscopy combined with the low-temperature matrix-isolation technique. The most stable dithione–diamino tautomer of the compound was exclusively observed in argon matrixes immediately after deposition. Upon UV ( $\lambda > 345$  nm) irradiation the dithione–diamino form transformed, by a double-proton transfer, into the dithiol–diimino tautomer. Theoretically supported analysis of the infrared spectrum emerging upon UV irradiation allowed identification of one of the conformers of the dithiol–diimino tautomer as the dominating photoproduct. Smaller quantities of other conformers of the dithiol–diimino tautomer were also found to be photogenerated. For the UV-irradiated matrix kept subsequently at 10 K and in darkness, a dithiol–diimino  $\rightarrow$  dithione–diamino tautomerization leading to partial recovery of the initial form of the compound was observed. The only possible mechanism of this ground-state transformation at cryogenic temperature is synchronous double-proton tunneling. The experimentally obtained time constant of this process was 18 h.

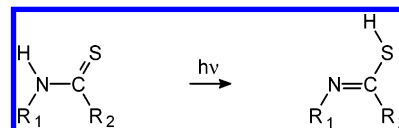
## Introduction

Phototautomeric reactions converting the thione–amino forms of simple thioamides, such as thiourea<sup>1</sup> and thioacetamide,<sup>2</sup> into the corresponding thiol–imino isomers were recently observed for compounds isolated in low-temperature inert gas matrixes. Intramolecular thione  $\rightarrow$  thiol phototransformations were also observed for some heterocyclic compounds: 2(1*H*)-pyridinethione,<sup>3</sup> 2(1*H*)-quinolinethione,<sup>4</sup> 3(2*H*)-pyridazinethione, and 4(3*H*)-pyrimidinethione.<sup>5</sup> In all cases, a proton was transferred from the NH group to the sulfur atom of the thiocarbonyl group placed in the  $\alpha$  position with respect to the nitrogen atom (Scheme 1). So far, UV-induced double-proton-transfer processes have been reported for only two molecules: 2,4-dithiouracil<sup>6</sup> and 2,6-dithiopurine.<sup>7</sup> Notably, in the latter case the dominating photoprocess corresponded to proton transfer from the  $\beta$  position (Scheme 2).

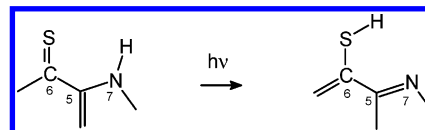
The molecule of dithiooxamide (DTO) is built of two thioamide units connected by a single C–C bond (Chart 1). It was demonstrated<sup>8</sup> that in the crystalline state the compound adopts the dithione–diamino tautomeric form (shown in Chart 1). On considering this structure of DTO, it is easy to notice that, in principle, proton transfers are possible from amino groups to the thiocarbonyl groups placed at  $\alpha$  and  $\beta$  positions.

Recently, an unusual occurrence of thiol  $\rightarrow$  thione ground-state proton tunneling through a very high energy barrier (ca. 105 kJ mol<sup>−1</sup>) was observed for matrix-isolated thiourea<sup>1</sup> at 10 K. During this process the photoproduct thiol form of thiourea was transformed back into the initial thione form of the compound. The time constant of this conversion was 52 h. As far as we know, this observation of proton tunneling through

## SCHEME 1: UV-Induced Proton Transfer to the Sulfur Atom in the $\alpha$ Position<sup>1–5</sup>

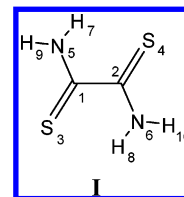


## SCHEME 2: UV-Induced Proton Transfer from the N–H Group to the Sulfur Atom in the $\beta$ Position<sup>a,7</sup>



<sup>a</sup> The numbers refer to the standard atom numbering in purines.

## CHART 1: Dithione–Diamino Tautomer I of Dithiooxamide<sup>a</sup>



<sup>a</sup> According to MP2/6-311++G(2d,p) calculations, this form is planar with  $C_{2h}$  symmetry.

such a high barrier was unprecedented. Very recently, an analogous (selenol  $\rightarrow$  selenone) proton-tunneling process has been reported for selenourea.<sup>9</sup> In that case, the barrier for the ground-state selenol  $\rightarrow$  selenone tautomerization was somewhat lower (ca. 95 kJ mol<sup>−1</sup>) and the tunneling process was faster (time constant 16 h). As far as isolated, monomeric molecules are concerned, no other example of proton tunneling through barriers of comparable height has previously been reported.

\* To whom correspondence should be addressed. E-mail: mjanowak@ifpan.edu.pl.

<sup>†</sup> Polish Academy of Sciences.

<sup>‡</sup> University of Coimbra.

**TABLE 1: Symmetry Coordinates Used in the Normal-Mode Analysis for the Dithione–Diamino Tautomer I of Dithiooxamide<sup>a</sup>**

definition	symmetry	symbol
$S_1 = (2^{-1/2})(r_{1,3} - r_{2,4})$	B <sub>u</sub>	$\nu(\text{C}=\text{S})$
$S_2 = (2^{-1/2})(r_{1,5} - r_{2,6})$	B <sub>u</sub>	$\nu(\text{CN})$
$S_3 = (2^{-1/2})(r_{5,9} - r_{6,10})$	B <sub>u</sub>	$\nu_1(\text{NH})$
$S_4 = (2^{-1/2})(r_{5,7} - r_{6,8})$	B <sub>u</sub>	$\nu_2(\text{NH})$
$S_5 = (1/2)(\beta_{4,1,2} - \beta_{4,6,2} - \beta_{3,2,1} + \beta_{3,5,1})$	B <sub>u</sub>	$\beta(\text{C}=\text{S})$
$S_6 = (1/2)(\beta_{6,1,2} - \beta_{6,4,2} - \beta_{5,2,1} + \beta_{5,3,1})$	B <sub>u</sub>	$\beta(\text{CN})$
$S_7 = (12^{-1/2})(2\beta_{7,9,5} - \beta_{7,1,5} - \beta_{9,1,5} - 2\beta_{8,10,6} + \beta_{8,2,6} + \beta_{10,2,6})$	B <sub>u</sub>	scis NH <sub>2</sub>
$S_8 = (1/2)(\beta_{9,1,5} - \beta_{7,1,5} - \beta_{10,2,6} + \beta_{8,2,6})$	B <sub>u</sub>	rock NH <sub>2</sub>
$S_9 = (8^{-1/2})(\tau_{9,5,1,2} + \tau_{9,5,1,3} + \tau_{7,5,1,2} + \tau_{7,5,1,3} + \tau_{10,6,2,1} + \tau_{10,6,2,4} + \tau_{8,6,2,1} + \tau_{8,6,2,4})$	A <sub>u</sub>	twist NH <sub>2</sub>
$S_{10} = (2^{-1/2})(\gamma_{1,7,5,9} + \gamma_{2,8,6,10})$	A <sub>u</sub>	wag NH <sub>2</sub>
$S_{11} = (2^{-1/2})(\gamma_{2,5,1,3} + \gamma_{1,6,2,4})$	A <sub>u</sub>	wag thioamide
$S_{12} = (1/2)(\tau_{4,2,1,3} + \tau_{4,2,1,5} + \tau_{6,2,1,3} + \tau_{6,2,1,5})$	A <sub>u</sub>	twist C–C

<sup>a</sup> Atom numbering as in Chart 1. Symmetry coordinates belonging to the A<sub>g</sub> and B<sub>g</sub> representations are not included. Normal modes with A<sub>g</sub> or B<sub>g</sub> symmetry are not active in IR.  $r_{ij}$  is the distance between atoms A<sub>i</sub> and A<sub>j</sub>.  $\beta_{i,j,k}$  is the angle between vectors A<sub>k</sub>A<sub>i</sub> and A<sub>k</sub>A<sub>j</sub>.  $\tau_{i,j,k,l}$  is the dihedral angle between the plane defined by the A<sub>i</sub>, A<sub>j</sub>, and A<sub>k</sub> atoms and the plane defined by the A<sub>j</sub>, A<sub>k</sub>, and A<sub>l</sub> atoms.  $\gamma_{i,j,k,l}$  is the angle between the vector A<sub>k</sub>A<sub>i</sub> and the plane defined by atoms A<sub>j</sub>, A<sub>k</sub>, and A<sub>l</sub>.

In the present paper, the UV-induced dithione → dithiol double-proton-transfer reaction in matrix-isolated DTO is reported. Observation of the ground-state dithiol → dithione double-proton tunneling, leading to recovery of the initial dithione form, is also accounted for. We are not aware of any reports on similar cases of synchronous double-proton tunneling.

## Experimental Section

The sample of dithiooxamide (98%) was obtained from Aldrich and used without further purification. To deposit the matrix, crystalline DTO was electrically heated in a miniature glass oven placed in the vacuum chamber of a continuous flow helium cryostat. The vapors of the compound were frozen together with a large excess of an inert gas on a CsI window cooled to 10 K. The argon matrix gas was of spectral purity, as supplied by Linde AG. Infrared spectra were recorded in the range 4000–200 cm<sup>−1</sup>, at 0.5 cm<sup>−1</sup> resolution, using a Thermo Nicolet Nexus 670 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 light from the HBO200 high-pressure mercury lamp fitted with a water filter and a cutoff filter transmitting light with  $\lambda > 345$  nm. The typical irradiation time was 1 h.

## Computational Details

The molecular geometries of isomers of DTO were optimized at the density functional theory (DFT(B3LYP)) level, with Becke’s three-parameter exchange functional and gradient-corrected functional of Lee, Yang, and Parr.<sup>10–12</sup> The standard 6-31++G(d,p) basis set<sup>13</sup> was used in these calculations. Harmonic vibrational frequencies and IR intensities were then calculated at the optimized geometries. To correct for systematic shortcomings of the applied methodology (mainly for anharmonicity), the predicted vibrational wavenumbers were scaled down with a single factor of 0.98. The standard potential energy distribution (PED) analysis<sup>14</sup> of the calculated normal modes was performed. The symmetry coordinate system used in this analysis is presented in Tables 1 and 3 (see also Table S1 in the Supporting Information).

The barrier for concerted double-proton transfer in the electronic ground state was calculated using the minimum energy path approach. At each of the points intermediate between the dithiol–diimino and dithione–diamino tautomeric forms, all geometry parameters (except for the driving coordi-

nate) were optimized, with conservation of the C<sub>2h</sub> symmetry, using the MP2 method<sup>15,16</sup> and the 6-311++G(2d,p) basis set. The GAUSSIAN 98 program<sup>17</sup> was used in all the cases.

## Results and Discussion

**Dithiooxamide Monomers.** Thione–amino tautomeric forms of simple thioamides (thioformamide, thioacetamide, thiourea) are more stable than thiol–imino forms. Theoretical calculations predict for these compounds energy differences between the thione–amino and thiol–imino tautomers as large as 39–55 kJ mol<sup>−1</sup>.<sup>1,2,18</sup> Such a significant energy difference prohibits thermal population of thioamide isomers other than the most stable tautomer. Indeed, only the thione–amino forms of simple thioamides were experimentally observed until very recently, when photochemical generation of thiol–imino tautomers was reported.<sup>1,2</sup>

Tautomerism of DTO follows the general pattern known from previous studies of the simplest thioamides. The dithione–diamino planar structure **I**, with overall symmetry C<sub>2h</sub> (Chart 1), is theoretically predicted to be the most stable form of the compound. This isomer is stabilized by four intramolecular, hydrogen-bond-like interactions. Moreover, in structure **I** repulsion between the lone electron pairs of the sulfur atoms (as well as repulsion between the hydrogen atoms) is minimal. No further minima could be located on the potential energy surface of the dithione–diamino tautomer of DTO. In particular, the structure with the sulfur atoms on the same side of the C–C bond was found to be a saddle point lying 77 kJ mol<sup>−1</sup> (DFT(B3LYP)/6-31++G(d,p)) above the stable conformer **I**, whereas all structures exhibiting a nonplanar arrangement around the C–C bond were found to converge upon optimization to the most stable, planar form **I**.

Other tautomers of DTO are much higher in energy. The second most stable form of the compound, conformer **II** (Chart 2) of the dithiol–diimino tautomer, was predicted to be energetically higher by 85.3 kJ mol<sup>−1</sup>, with respect to isomer **I**. The relative energy of these isomers was calculated at the MP2/6-311++G(2d,p) level and corrected for zero-point vibrational energy using the normal-mode frequencies computed at the DFT(B3LYP)/6-31++G(d,p) level. The experimental infrared spectrum of DTO isolated in an Ar matrix is presented in Figure 1. This spectrum is compared with the results of a theoretical simulation carried out at the DFT(B3LYP)/6-31++G(d,p) level for form **I**. The symmetry of the molecule reduces the number of infrared active modes to 12. The agreement between the experimental and theoretical spectra is

**TABLE 2: Experimental Wavenumbers ( $\tilde{\nu}/\text{cm}^{-1}$ ) and Relative Integral Intensities ( $I$ ) of the Absorption Bands of Matrix-Isolated Dithiooxamide, Compared with the Wavenumbers ( $\tilde{\nu}/\text{cm}^{-1}$ ), Absolute Intensities [ $A^{\text{th}}/(\text{km mol}^{-1})$ ], and Potential Energy Distribution (PED/%) Theoretically Calculated for the Dithione–Diamino Form I of the Compound**

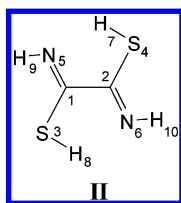
experimental, Ar matrix		calculated, DFT(B3LYP)/6-31++G(d, p)		
$\tilde{\nu}^a$	$I$	$\tilde{\nu}^b$	$A^{\text{th}}$	PED <sup>c</sup>
3494/3491	294	3619	209	$\nu_1(\text{NH})$ (87), $\nu_2(\text{NH})$ (14)
3277/3273	329	3414	215	$\nu_2(\text{NH})$ (86), $\nu_1(\text{NH})$ (13)
1547/1537	428	1566	490	scis $\text{NH}_2$ (80), $\nu(\text{CN})$ (19)
1394/1392	310	1388	301	$\nu(\text{CN})$ (72), scis $\text{NH}_2$ (19)
1381	38			
1344	31			
1276	4			
1266	7			
1258/1256	25			
1237	5			
1224	52	1207	134	rock $\text{NH}_2$ (76), $\beta(\text{CN})$ (11)
1154	4			
1150	2			
1119/1116/1113	87			
1048/1043	74			
891	5			
863/860/856/852	61	847	60	$\nu(\text{C}=\text{S})$ (77), rock $\text{NH}_2$ (17)
640/639	12	647	17	twist $\text{NH}_2$ (94)
524/523	219	505	278	wag $\text{NH}_2$ (86), wag thioamide (14)
448	1	449	1	$\beta(\text{CN})$ (67), $\beta(\text{C}=\text{S})$ (19)
389/386	33	382	50	wag thioamide (86), wag $\text{NH}_2$ (11)
283/282	27	270	26	$\beta(\text{C}=\text{S})$ (78), $\beta(\text{CN})$ (21)
		48	7	twist C–C (102)

<sup>a</sup> Wavenumbers of the strongest bands are italic. <sup>b</sup> Theoretical wavenumbers were scaled by a factor of 0.98. <sup>c</sup> PEDs lower than 10% are not included. Symmetry coordinates used in the normal-mode analysis are given in Table 1.

**TABLE 3: Symmetry Coordinates Used in the Normal-Mode Analysis for Conformer II of the Dithiol–Diimino Tautomer of Dithiooxamide<sup>a</sup>**

definition	symmetry	symbol
$S_1 = r_{1,3} - r_{2,4}$	B <sub>u</sub>	$\nu(\text{CS})$
$S_2 = r_{1,5} - r_{2,6}$	B <sub>u</sub>	$\nu(\text{C}=\text{N})$
$S_3 = r_{5,9} - r_{6,10}$	B <sub>u</sub>	$\nu(\text{NH})$
$S_4 = r_{3,8} - r_{4,7}$	B <sub>u</sub>	$\nu(\text{SH})$
$S_5 = \beta_{4,1,2} - \beta_{4,6,2} - \beta_{3,2,1} + \beta_{3,5,1}$	B <sub>u</sub>	$\beta(\text{CS})$
$S_6 = \beta_{6,1,2} - \beta_{6,4,2} - \beta_{5,2,1} + \beta_{5,3,1}$	B <sub>u</sub>	$\beta(\text{C}=\text{N})$
$S_7 = \beta_{10,2,6} - \beta_{9,1,5}$	B <sub>u</sub>	$\beta(\text{NH})$
$S_8 = \beta_{8,1,3} - \beta_{7,2,4}$	B <sub>u</sub>	$\beta(\text{SH})$
$S_9 = \tau_{9,5,1,2} + \tau_{9,5,1,3} + \tau_{10,6,2,1} + \tau_{10,6,2,4}$	A <sub>u</sub>	$\tau(\text{NH})$
$S_{10} = \tau_{8,3,1,2} + \tau_{8,3,1,5} + \tau_{7,4,2,1} + \tau_{7,4,2,6}$	A <sub>u</sub>	$\tau(\text{SH})$
$S_{11} = \gamma'_{2,5,1,3} + \gamma'_{1,6,2,4}$	A <sub>u</sub>	wag thioamide
$S_{12} = \tau_{4,2,1,3} + \tau_{4,2,1,5} + \tau_{6,2,1,3} + \tau_{6,2,1,5}$	A <sub>u</sub>	twist C–C

<sup>a</sup> Atom numbering as in Chart 2. Symmetry coordinates belonging to the A<sub>g</sub> and B<sub>g</sub> representations are not included. Normal modes with A<sub>g</sub> or B<sub>g</sub> symmetry are not active in IR.  $r_{ij}$  is the distance between atoms A<sub>i</sub> and A<sub>j</sub>.  $\beta_{i,j,k}$  is the angle between vectors A<sub>i</sub>A<sub>j</sub> and A<sub>k</sub>A<sub>j</sub>.  $\tau_{i,j,k,l}$  is the dihedral angle between the plane defined by the A<sub>i</sub>, A<sub>j</sub>, and A<sub>k</sub> atoms and the plane defined by the A<sub>j</sub>, A<sub>k</sub>, and A<sub>l</sub> atoms.  $\gamma'_{i,j,k,l}$  is the angle between the vector A<sub>k</sub>A<sub>i</sub> and the plane defined by atoms A<sub>j</sub>, A<sub>k</sub>, and A<sub>l</sub>.

**CHART 2: Conformer II of the Dithiol–Diimino Tautomer of DTO<sup>a</sup>**

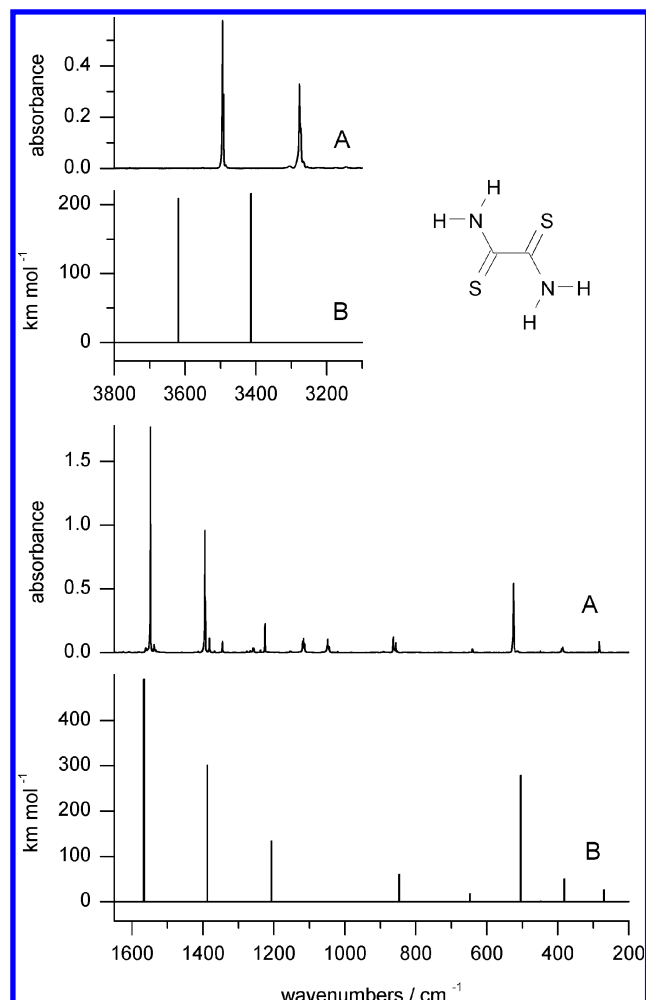
<sup>a</sup> According to MP2/6-311++G(2d,p) calculations, this form is planar with C<sub>2h</sub> symmetry.

seen to be very good, allowing reliable assignment of the observed bands (Table 2; see also Table S2 in the Supporting Information). The small features at 1381, 1258, 1116, and 1048

cm<sup>−1</sup>, which have no counterparts in normal modes calculated in a harmonic approximation, can be caused by combinational modes or symmetry breaking due to matrix effects.

The strongest band in the spectrum is observed at 1547 cm<sup>−1</sup> and is ascribed to the scissoring mode of the amino groups that is predicted at 1566 cm<sup>−1</sup>. The bands corresponding to the rocking, twisting, and wagging deformations of these groups were found at 1224, 640, and 524 cm<sup>−1</sup>, respectively (predicted values: 1207, 647, and 505 cm<sup>−1</sup>). The last frequency is considerably higher than that of the band due to the analogous vibration in thioacetamide,<sup>2</sup> which is only 368 cm<sup>−1</sup>. The high frequency of the amino group wagging mode indicates a more pronounced interaction of NH hydrogen atoms with the sulfur lone electron pairs (S<sub>lp</sub>) in DTO in comparison with the corresponding interaction in thioacetamide. There are two reasons for this: first, each of the amino groups in DTO has two C=S neighbors, while in simple monothioamides there is only one C=S neighbor; second, the N(5)H(7)⋯S(4)<sub>lp</sub> and N(6)H(8)⋯S(3)<sub>lp</sub> interactions closing the five-membered rings in DTO (see Chart 1) are stronger than the N(6)H(10)⋯S(4)<sub>lp</sub> and N(5)H(9)⋯S(3)<sub>lp</sub> interactions in the four-membered rings typical of simple thioamides. In the structure of form I optimized at the MP2/6-311++G(2d,p) level, the H(7)⋯S(4) distance is 2.399 Å, whereas the H(10)⋯S(4) distance is 2.811 Å.

The stronger NH⋯S<sub>lp</sub> interaction observed in DTO is also revealed by the unusual coupling of the NH stretching vibrations. Instead of the typical “symmetric” and “antisymmetric” coupling of the individual NH oscillators of each amino group (which is usually observed for simple amides and thioamides), in DTO the NH stretching vibrations of the hydrogen atoms that are interacting with the sulfur lone electron pairs through five-membered rings are coupled with each other and give rise to an infrared band observed at 3277 cm<sup>−1</sup>. The low frequency of this vibration indicates a relatively strong hydrogen-bond-like intramolecular interaction. In turn, the band observed at a higher frequency (3494 cm<sup>−1</sup>) is due to the NH stretching vibrations of the hydrogen atoms that interact with the sulfur lone electron

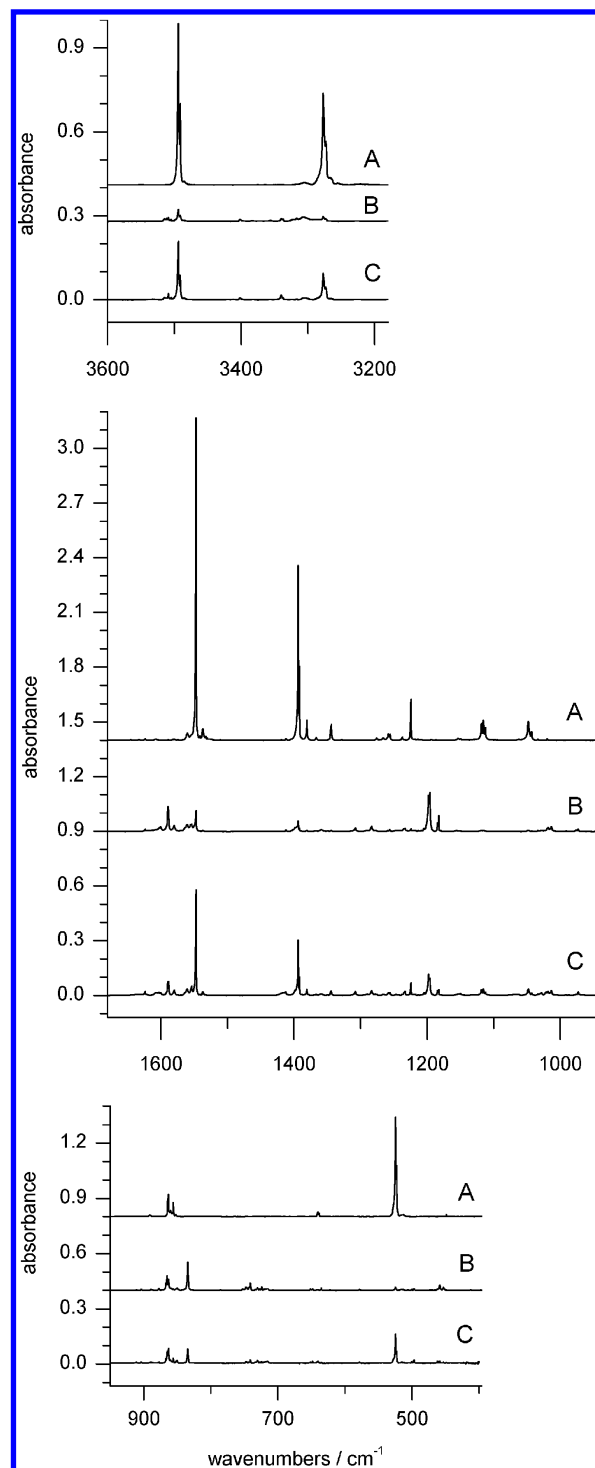


**Figure 1.** Infrared spectra of dithiooxamide: (A) isolated in an Ar matrix; (B) theoretically predicted at the DFT(B3LYP)/6-31++G(d,p) level for the dithione tautomeric form. Theoretical wavenumbers were scaled by 0.98.

pairs through four-membered rings. This demonstrates that the  $\text{NH}\cdots\text{S}_{\text{ip}}$  interactions closing the four-membered ring are significantly weaker.

**Double-Proton-Transfer Processes.** After 1 h of UV ( $\lambda > 345$  nm) irradiation of the matrix, the initial IR spectrum disappeared almost completely, whereas new bands due to photoproduct(s) emerged (Figure 2). The characteristic features of the new spectrum are low intensities of the emerged bands, appearance of new bands in the 2610–2500 cm<sup>-1</sup> region (typical frequency range of stretching SH vibrations, shown in Figure 3), and almost total disappearance of IR absorptions in the 3500–3250 cm<sup>-1</sup> range (the NH stretching region). This suggests that UV irradiation promoted transformation of the dithione–diamino tautomer of DTO into the dithiol–diimino isomer(s). Note that the bands due to NH stretching vibrations of an imino group are always much less intense than the bands caused by NH stretching vibrations of an amino group.<sup>1,2,9</sup>

An important characteristic of the spectrum of the main photoproduct(s) is the band due to the stretching vibrations of the SH groups [ $\nu(\text{SH})$ ] found at 2521 cm<sup>-1</sup> (Figure 3). The frequency of this band is lower and its intensity is higher than usually found for other matrix-isolated thiol molecules. For example, the bands due to SH stretching vibrations in the photogenerated thiol–imino forms of thiourea and thioacetamide were found at 2625 and 2607 cm<sup>-1</sup>, respectively.<sup>1,2</sup> Typical intensities of  $\nu(\text{SH})$  bands are so low that these absorptions are

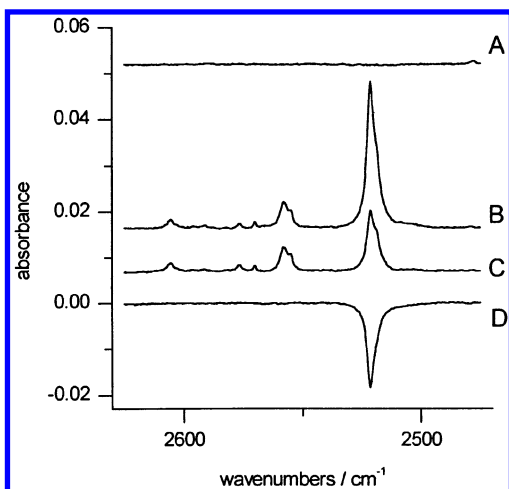


**Figure 2.** Infrared spectra of dithiooxamide isolated in an Ar matrix: (A) after deposition of the matrix; (B) after 1 h of UV ( $\lambda > 345$  nm) irradiation; (C) after subsequent 24 h of keeping the matrix at 10 K and in darkness.

hardly detectable. The unusually low frequency and relatively high intensity of the  $\nu(\text{SH})$  band observed in the photoproduct generated from DTO strongly suggest that in this species the SH groups are involved in an intramolecular hydrogen-bond-like interaction.

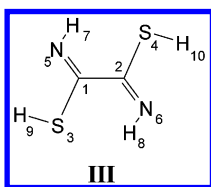
Theoretical geometry optimizations revealed that there are 10 stable dithiol–diimino conformers with the sulfur atoms in trans positions with respect to each other and 7 stable conformers with these atoms in the cis orientation (Chart S1 in the Supporting Information). The calculated relative energies of





**Figure 3.**  $\nu(\text{SH})$  range of the IR spectra of dithiooxamide: (A) after deposition of the matrix; (B) after 1 h of UV ( $\lambda > 345$  nm) irradiation; (C) after subsequent 24 h of keeping the matrix at 10 K and in darkness; (D) spectrum C minus spectrum B.

### CHART 3: Conformer III of the Dithiol–Diimino Tautomer of DTO<sup>a</sup>



<sup>a</sup> According to MP2/6-311++G(2d,p) calculations, both H–N=C–S–H units are quasi-planar, but they are twisted with respect to each other. The molecule has  $C_2$  symmetry. The N=C–C=N dihedral angle is  $144.0^\circ$ .

these conformers are collected in Table S3 (Supporting Information). Among the possible conformers of the dithiol–diimino tautomer of DTO only in form **II** (presented in Chart 2), both SH groups are involved in a comparatively strong hydrogen-bond-like interaction. In the  $C_{2h}$  structure of form **II** the N(5)···H(7)–S distance is 2.080 Å. The N···H–S intramolecular interaction which closes the five-membered ring is considerably stronger than the analogous interaction in the thiol–imino tautomers of simple monothioamides (where an energetically less favorable four-membered ring is formed). Indeed, the N···H–S distances in the thiol tautomers of thioacetamide and thioformamide are 2.515 and 2.559 Å, respectively. Similarly, the N(5)···H(9)–S distance in conformer **III** (Chart 3) of the dithiol–diimino tautomer of DTO, where N···H–S interactions closing the four-membered ring are analogous to those in thiol–imino tautomers of simple thioamides, was predicted to be 2.522 Å. All distances quoted above concern geometries optimized at the MP2/6-311++G(2d,p) level.

The low frequency and the higher than usual intensity of the  $\nu(\text{SH})$  band in the spectrum of the photoproduct species are well reproduced in the theoretically predicted spectrum for conformer **II** (see Table 4). The calculated frequency (2562  $\text{cm}^{-1}$ ) is significantly lower and the calculated intensity (145  $\text{km mol}^{-1}$ ) is much higher in comparison with the corresponding values calculated for the thiol–imino form of thiourea (2668  $\text{cm}^{-1}$  and 1  $\text{km mol}^{-1}$ ) or the thiol–imino form of thioacetamide (2641  $\text{cm}^{-1}$  and 1  $\text{km mol}^{-1}$ ).<sup>1,2</sup> Similar values (2639  $\text{cm}^{-1}$  and 1  $\text{km mol}^{-1}$ ) were also obtained for conformer **III**.

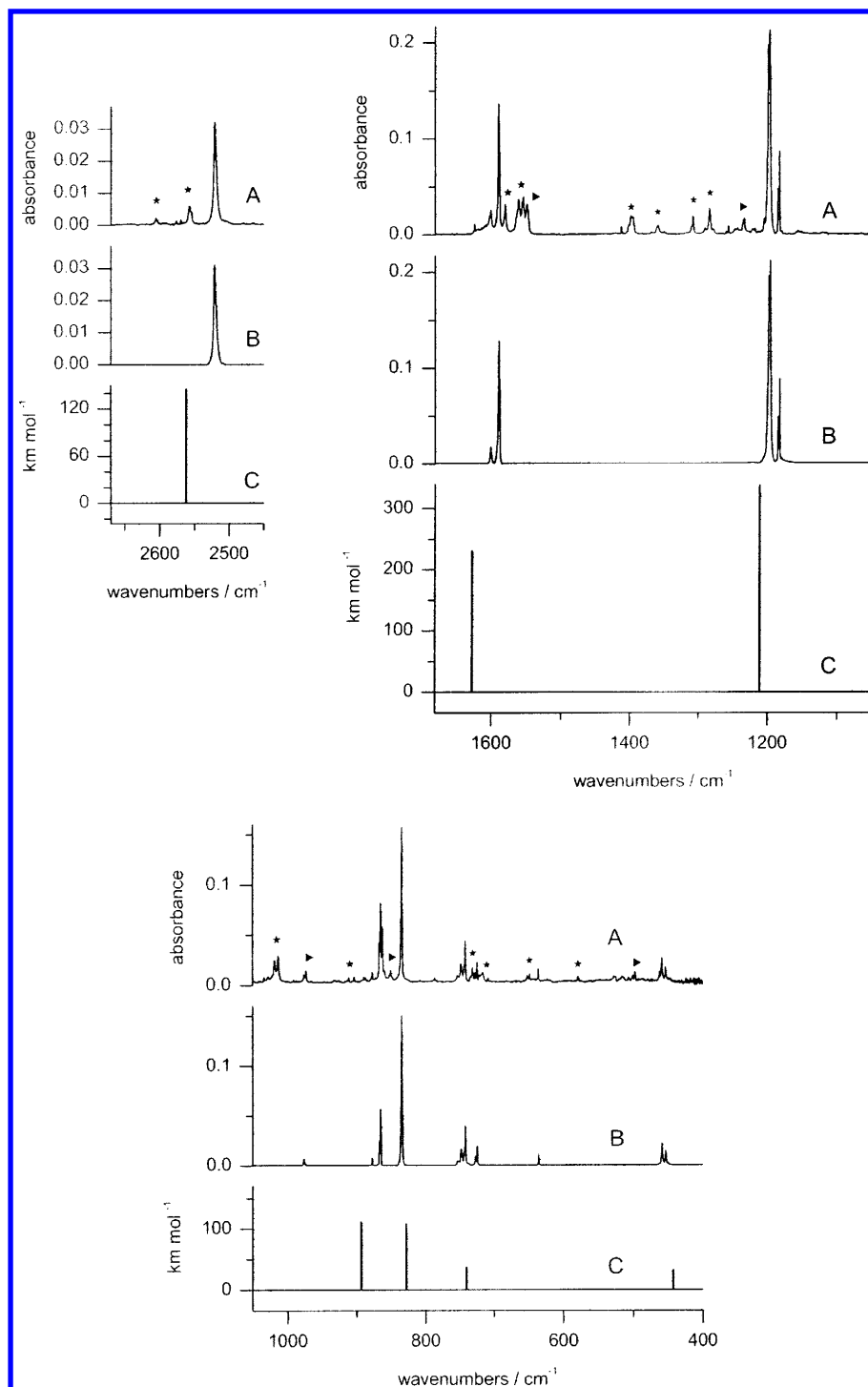
The UV-irradiated matrix was subsequently left at 10 K and in darkness. The infrared beam of the FTIR spectrometer and HeNe laser beam were blocked during this period. Over 24 h a

**TABLE 4: Experimental Wavenumbers ( $\tilde{\nu}/\text{cm}^{-1}$ ) and Relative Integral Intensities ( $I$ ) of the Absorption Bands of Photoproducts Generated upon UV ( $\lambda > 345$  nm) Irradiation of Matrix-Isolated Dithiooxamide, Compared with the Wavenumbers ( $\tilde{\nu}/\text{cm}^{-1}$ ), Absolute Intensities [ $A^{\text{th}}/(\text{km mol}^{-1})$ ], and Potential Energy Distribution (PED/%) Theoretically Calculated for Conformer II of the Dithiol–Diimino Tautomer of the Compound**

experimental, Ar matrix		calculated, DFT(B3LYP)/6-31++G(d, p)		
$\tilde{\nu}^a$	$I$	$\tilde{\nu}^b$	$A^{\text{th}}$	PED <sup>d</sup>
3515	11 –			
3511	11 ↓			
3509	9 ↑			
3505	5 ↑			
3401	10 –			
		3438	21	$\nu(\text{NH})$ (98)
3356	5 ↓			
3340	12 ↑			
3337	7 ↓			
3307	84 ↓			
2605	3 –			
2577	4 –			
2570	1 –			
2558	11 –			
2521	71 ↓	2562	145	$\nu(\text{SH})$ (100)
1603	18 –			
1601/1589	191 ↓	1627	231	$\nu(\text{C}=\text{N})$ (96)
1580	52 –			
1561	76 –			
1556	29 ↓			
1554	43 ↑			
1397	47 –			
1359	12 –			
1308	18 –			
1284	48 –			
1235	12 –			
1233	14 ↑			
1198/1196/1184/1183	427 ↓	1211	338	$\beta(\text{NH})$ (85)
1018/1013	66 –			
976	6 ↓			
973	8 ↑			
911	3 –			
904	3 –			
877	4 ↓			
867/865	80 ↓	894	111	$\beta(\text{SH})$ (80), $\beta(\text{NH})$ (12)
850	17 ↑			
834	132 ↓	828	108	$\tau(\text{NH})$ (94)
747/741/727/ 724	81 ↓	740	37	$\nu(\text{CS})$ (75), $\beta(\text{C}=\text{N})$ (17)
730	16 –			
715	22 –			
651	6 –			
648	5 –			
635	7 ↓			
578	3 –			
500	6 –			
497	7 ↑			
462	7 –			
458/453	33 ↓	443	32	$\beta(\text{C}=\text{N})$ (88)
		384	55	$\tau(\text{SH})$ (62), wag thioamide (36)
365	16 ↓	365	11	wag thioamide (60), $\tau(\text{SH})$ (36)
293	16			
228	9 ↓	247	26	$\beta(\text{CS})$ (98)
		68	0.4	twist C–C (99)

<sup>a</sup> Wavenumbers of the strongest bands are italic. <sup>b</sup> Theoretical wavenumbers were scaled by a factor of 0.98. <sup>c</sup> Bands of the photoproducts: ↓, decreasing; ↑, increasing; –, unchanged during the period when the matrix was kept in darkness and at 10 K. <sup>d</sup> PEDs lower than 10% are not included. Symmetry coordinates used in the normal-mode analysis are given in Table 3.

systematic recovery of the initial dithione–diamino form **I** of DTO was observed (see Figure 2). This process was accompanied by the decrease of a set of bands in the spectrum due to the photoproduct(s). The most intense bands that appeared after UV irradiation belong to this set. These bands, as well as all other bands that were intense enough to allow measurement of the time evolution of their decline, decreased at the same rate. However, not all bands that appeared after UV irradiation



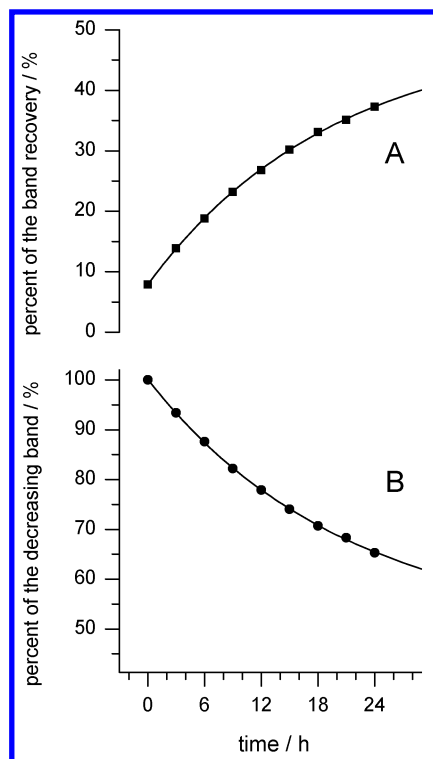
**Figure 4.** (A) Infrared spectrum of photoproducts generated upon UV ( $\lambda > 345$  nm) irradiation of dithiooxamide isolated in an Ar matrix. Bands of the main photoproduct are not marked (all these bands decay at the same rate during the tunneling back to form **I**). Bands marked with an asterisk do not change their intensities; those marked with a solid arrow grow during this period. (B) Extracted spectrum of the bands due to the main photoproduct. (C) Theoretically predicted spectrum (at the DFT(B3LYP)/6-31++G(d,p) level) for conformer **II** of the dithiol tautomer of dithiooxamide. Theoretical wavenumbers were scaled by a factor of 0.98.

decreased during the time when the matrix was kept in darkness. Some of the least intense bands increased in intensity, whereas some others did not change at all (see Table 4, Figure 4, and Figure S1). Among the bands belonging to the last category, those found at 2605, 2577, 2570, and 2558  $\text{cm}^{-1}$  indicate that, alongside the main dithiol–diimino photoproduct with the characteristic  $\nu(\text{SH})$  band at 2521  $\text{cm}^{-1}$ , several other dithiol–diimino conformers were also photogenerated (see Figure 3).

Equal rates of decrease during the period when the matrix was kept in darkness allowed for positive identification of the

bands belonging to the spectrum of the main photoproduct. The extracted spectrum of those bands is well reproduced by the calculated spectrum of the dithiol–diimino conformer **II**. The graphical comparison presented in Figure 4 (see also Table 4) strongly supports the assignment of the main photoproduct to form **II**.

While the UV-irradiated matrix was kept in darkness, the recovery of the dithione–diamino form of DTO was periodically monitored. After 24 h the IR bands of the dithione–diamino tautomer regained 32% of their initial intensities recorded just



**Figure 5.** (A) Progress of the recovery of the dithione tautomer **I** of dithiooxamide measured as the intensity increase of the band at 1547  $\text{cm}^{-1}$ . A value of 100% corresponds to the intensity of the band before UV irradiation. (B) Decrease of the band at 1589  $\text{cm}^{-1}$ , from the spectrum of form **II**, as a function of time. A value of 100% corresponds to the intensity of the band immediately after irradiation. For both panels, the time scale begins at the moment when the UV irradiation ceased.

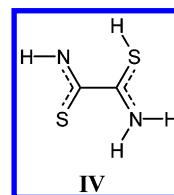
after deposition of the matrix. The recovery of the representative band at 1547  $\text{cm}^{-1}$  is presented in Figure 5A as a function of time. The time constant for the dithiol–diimino  $\rightarrow$  dithione–diamino process, obtained from the fit of the function  $y = y_0 + A(1 - e^{-kt})$  to the experimental points shown in Figure 5A, is 18 h. The time evolution of the decreasing bands due to form **II**, during the period of 24 h of keeping the matrix in darkness, is presented in Figure 5B. The rate of decrease of these bands is the same as the rate of increase of the bands due to dithione–diamino tautomer **I**. This shows that the major tunneling process **II**  $\rightarrow$  **I** is not significantly perturbed by any other isomerization occurring in darkness.

### Concluding Discussion

In the present study, two proton-transfer processes leading to transformation between isomers **I** and **II** of DTO were observed. One of these processes corresponds to UV-induced double-proton transfer, **I**  $\rightarrow$  **II**. Upon electronic excitation two protons are transferred from the nitrogen atoms to the sulfur atoms placed in the  $\beta$  positions.

The other process is the ground-state **II**  $\rightarrow$  **I** tautomerism occurring in the dark. A barrier for transformation of the dithiol–diimino isomer **II** into the dithione–diamino tautomer **I**, by concerted movement of two protons in the electronic ground state, was theoretically assessed (at the MP2/6-311++-(2d,p) level) using the minimum energy path approach. Those calculations predicted a barrier height of 23  $\text{kJ mol}^{-1}$ . At cryogenic temperature (10 K), thermal isomerization over such a barrier is very unlikely. Therefore, the only possible mechanism of the ground-state **II**  $\rightarrow$  **I** tautomerization is proton

### CHART 4: Conformation IV of Dithiooxamide



tunneling.<sup>19</sup> Two routes of such transformation could be considered: (i) stepwise tunneling of one and then of the other proton; (ii) simultaneous movement of both protons.

Stepwise transformation of dithiol–diimino isomer **II**, first into a thiol–thione isomer, **IV** (Chart 4), and then, in a second act, into the dithione–diamino form **I**, does not seem possible. The structure of the transient form **IV** is not canonical, and there is no minimum on the potential energy surface (PES) corresponding to such a configuration. The energies of the PES points around structure **IV** are higher by 60–80  $\text{kJ mol}^{-1}$  with respect to the dithiol–diimino isomer **II** (as results from calculations carried out at the MP2/6-311++G(2d,p) level). Hence, the energy conservation law should preclude stepwise tunneling of one proton (**II**  $\rightarrow$  **IV**) and then of the other (**IV**  $\rightarrow$  **I**) on the way from dithiol–diimino isomer **II** to the dithione–diamino tautomer **I**.

For single-proton-tunneling processes in thiourea and selenourea,<sup>1,9</sup> the calculated ground-electronic-state barriers (105  $\text{kJ mol}^{-1}$  for thiourea and 95  $\text{kJ mol}^{-1}$  for selenourea) are significantly higher than the barrier for double-proton transfer in DTO. Moreover, in DTO the distance for each of the protons to tunnel during the dithiol–diimino (**II**)  $\rightarrow$  dithione–diamino (**I**) transformation is only 1.1 Å, whereas for thiourea and selenourea the corresponding values are 2.2 and 2.3 Å, respectively. Although these two factors (barrier height and tunneling distance) are much more favorable in the case of DTO, the time constant (18 h) of the tunneling process is of the same order as those for thiourea and selenourea (52 and 16 h, respectively). This can be rationalized by taking into account the fact that the necessity of simultaneous crossing of the barrier by two protons in a single act must considerably lower the probability of such an event.

Proton-tunneling processes were previously observed also for other molecules (such as formic acid,<sup>20</sup> 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone,<sup>21</sup> and tetrachlorohydroquinone<sup>22</sup>) isolated in low-temperature matrixes. The calculated energy barriers for these processes were 33, 33, and 19  $\text{kJ mol}^{-1}$ , respectively. Although these values are quite similar to that calculated for DTO, the time constants of the proton-tunneling processes in formic acid and in the hydroquinones were dramatically shorter (varied from several minutes to less than 1 min). The drastic difference in the tunneling rates must be a consequence of the number of protons (two for DTO and one for the other compounds) involved in the process.

Concerted tunneling processes involving more than one proton are not unusual. Most popular are inversions of amino groups and rotations of methyl groups.<sup>23–25</sup> However, these are usually very quick occurrences in a symmetric or periodic potential. Apart from some analogies with these processes, the very slow dithiol–diimino  $\rightarrow$  dithione–diamino double-proton tunneling in isolated molecules of DTO is quite unique. As far as we are aware, the present observation of such a type of process is unprecedented.

**Acknowledgment.** This work was partially supported by the Portuguese Fundação para a Ciência e a Tecnologia (Research Project POCTI/QUI/43366/2001) and FEDER.



**Supporting Information Available:** Full set of symmetry coordinates used in the normal-mode analysis for the dithione–diamino tautomer **I** (Table S1), frequencies and forms of the normal modes calculated for this isomer (Table S2), structures of the stable conformers of the dithiol–diimino tautomer of DTO (Chart S1, Table S3), and fragments of the IR spectrum of DTO illustrating different patterns of behavior during the period of keeping the matrix at 10 K and in darkness (Figure S1). This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References and Notes

- (1) Rostkowska, H.; Lapinski, L.; Khvorostov A.; Nowak, M. J. *J. Phys. Chem. A* **2003**, *107*, 6373.
- (2) Lapinski, L.; Rostkowska, H.; Khvorostov A.; Nowak, M. J. *Phys. Chem. Chem. Phys.* **2003**, *5*, 1524.
- (3) Nowak, M. J.; Lapinski, L.; Rostkowska, H.; Les, A.; Adamowicz, L. *J. Phys. Chem.* **1990**, *94*, 7406.
- (4) Prusinowska, D.; Lapinski, L.; Nowak, M. J.; Adamowicz, L. *Spectrochim. Acta* **1995**, *51A*, 1809.
- (5) Nowak, M. J.; Lapinski, L.; Fulara, J.; Les, A.; Adamowicz, L. *J. Phys. Chem.* **1991**, *95*, 2404.
- (6) Lapinski, L.; Nowak, M. J.; Kolos, R.; Kwiatkowski, J. S.; Leszczynski, J. *Spectrochim. Acta, A* **1998**, *54*, 685.
- (7) Rostkowska, H.; Lapinski, L.; Nowak, M. J. *J. Phys. Chem. A* **2003**, *107*, 804.
- (8) Wheatley, P. J. *J. Chem. Soc.* **1965**, 1.
- (9) Rostkowska, H.; Lapinski, L.; Khvorostov, A.; Nowak, M. J. *Chem. Phys.* **2004**, *298*, 223.
- (10) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.
- (11) Lee, C. T.; Yang, W. T.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
- (12) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200.
- (13) Hariharan, P. C.; Pople, J. A. *Mol. Phys.* **1974**, *27*, 209.
- (14) Keresztury, G.; Jalsovszky, G. *J. Mol. Struct.* **1971**, *10*, 304.
- (15) Möller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.
- (16) Head-Gordon, M.; Pople, J. A.; Frisch, M. J. *J. Chem. Phys. Lett.* **1988**, *153*, 1988.
- (17) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Revision A.7.; Gaussian, Inc.: Pittsburgh, PA, 1998.
- (18) Dapprich, S.; Frenking, G. *Chem. Phys. Lett.* **1993**, *205*, 337.
- (19) Trommsdorff, H. P. *Adv. Photochem.* **1998**, *24*, 147.
- (20) Pettersson, M.; Maçõas, E. M. S.; Khriachtchev, L.; Lundell, J.; Fausto, R.; Räsänen, M. *J. Chem. Phys.* **2002**, *117*, 9095.
- (21) Akai, N.; Kudoh, S.; Takayanagi, M.; Nakata, M. *J. Phys. Chem. A* **2002**, *106*, 11029.
- (22) Akai, N.; Kudoh, S.; Nakata, M. *J. Phys. Chem. A* **2003**, *107*, 3655.
- (23) Lin, C. C.; Swalen, J. D. *Rev. Mod. Phys.* **1959**, *31*, 841.
- (24) Owen, N. L. *Studies of Internal Rotation by Microwave Spectroscopy*. In *Internal Rotation in Molecules*; Orville-Thomas, W. J., Ed.; John Wiley & Sons: London, New York, Sydney, Toronto, 1974; Chapter 6.
- (25) Howard, D. L.; Robinson, T. W.; Fraser, A. E.; Kjaergaard, H. G. *Phys. Chem. Chem. Phys.* **2004**, *6*, 719.