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# Interaction of thiazolidine-2-thione with 2,3,5,6-tetrabromo-1,4-benzoquinone: A set of sequential interactions involving redox and substitution reactions after an initial charge transfer complexation

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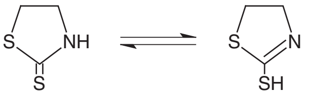
## ABSTRACT

Interaction between thiazolidine-2-thione (T2T) as an electron donor and 2,3,5,6-tetrabromo-1,4-benzoquinone (p-bromanil, BRL) as a π-electron acceptor has been studied by using several spectral techniques, viz. UV/visible, IR, $^1$H NMR and Mass spectra. A substitution reaction has been occurred after an initial formation of a CT complex, meanwhile a redox reaction has been occurred, in situ, too in which the interacting donor (T2T) has been oxidized to the corresponding thiazole. Thus, the stoichiometric ratio of this interaction has been found to be 2:1, T2T:BRL. However, the most interesting finding is that unexpectedly neither the SH group of the thiol form nor the NH group of the thione form of the T2T has shared in the substitution reaction with BRL. This finding has been confirmed by the different applied spectral tools, whereas a plausible reaction pathway has been illustrated and discussed.

## 1. Introduction

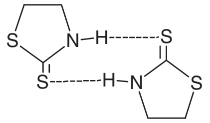
Due to the –(NH)–(C=S)– grouping and the electron donor properties of N and S atoms, thiazolidine-2-thione (T2T) and its derivatives have several pharmaceutical [1–11] and industrial applications [12–16]. Interactions of T2T as an electron donor with iodine as a σ-acceptor and DDQ as a π-acceptor have been reported [17,18]. However, according to our knowledge, yet to date no previous work has been reported for the interaction of T2T with other π-type acceptors viz. bromanil, chloranil, TCNE, TCNQ, etc. We have recently reported [17,18] that T2T has two tautomeric forms namely thione and thiol forms, Structures I and II, respectively. However, in the solid state, T2T exists [17,18] as a hydrogen-bonded thioamide complex (Structure III) formed between the NH of the thione form and the exocyclic sulfur atom.



( I )
Thione

( II )
Thiole

Structures (I) and (II): Thione–thiole tautomeres



Structure (III): Dimeric hydrogen-bonded thioamide complex

The complexity of this compound (T2T) and the willing to continue our studies [18–23] concerning the π-type acceptors have motivated us for this piece of work aiming to study the interaction of T2T with bromanil whether they undergo a CT complexation and/or a chemical reaction.

## 2. Experimental

### 2.1. Materials and solutions

The electron donor, thiazolidine-2-thione (T2T), was purchased from Aldrich Chemical Co. The electron acceptor,

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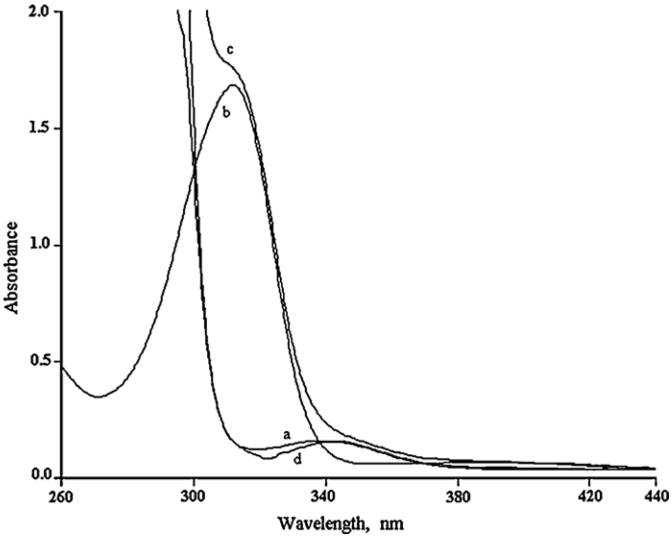


**Fig. 1.** Electronic absorption spectra of the $CH_2Cl_2$ solutions at 25 °C. (a) T2T solution; [T2T] = $1.0 \times 10^{-4}$ mol dm$^{-3}$, (b) BRL solution; [BRL] = $1.0 \times 10^{-4}$ mol dm$^{-3}$, (c) and (d) T2T–BRL mixture solution; [T2T] = $1.0 \times 10^{-4}$ mol dm$^{-3}$, [BRL] = $1.0 \times 10^{-4}$ mol dm$^{-3}$; where (c) blank = solvent; (d) blank = BRL.

2,3,5,6-tetrabromo-1,4-benzoquinone (BRL) (Aldrich Co.), was recrystallized from both chlorobenzene and dry methylene chloride. The solvents used were of pure spectral grade (BDH or E. Merck).

### 2.2. Physical measurements

The electronic absorption spectra were recorded on a Perkin-Elmer Lambda 40 spectrophotometer equipped with a Julabo FP 40 thermostat (±0.1 °C) using 1.0 cm matched quartz cells. IR spectra of the synthesized solid product were recorded on a Shimadzu IR-408 spectrophotometer. $^1$H NMR and Mass spectra measurements were carried out in the microanalytical laboratory, Cairo University.

### 2.3. Synthesis of the solid CT complex

The solid product of the interaction of T2T with BRL was synthesized by mixing the required amount of the donor (0.01 mol) in $CH_2Cl_2$ with an appropriate amount of the BRL (0.01 mol) in $CH_2Cl_2$ in the 1:1 mole ratio. The mixture was refluxed for 4 h. The resulted precipitate was separated by cooling the solution and it was washed several times with hexane. The synthesized solid product (T–B) has a faint green colour and its m.p. is 200 °C. T–B has been analyzed and investigated by several spectral techniques.

## 3. Results and discussion

### 3.1. Spectral study of the interaction between T2T and the π-acceptors

Electronic absorption spectra in the wavelength range of 250–750 nm were recorded for the mixture solutions of the T2T donor with the π-acceptor BRL in methylene chloride, cf. Fig. 1. The electronic spectra for these mixture solutions (T2T–BRL) did not show any new spectral band rather than those of the free donor (T2T) or the free acceptor (BRL), meanwhile all attempts to observe any CT band(s) for this interacting couple (T2T–BRL) were failed, cf. Fig. 1. However, as shown hereafter, examinations of the prepared solid product (T–B) resulting from the interactions of T2T with the acceptor BRL have indicated the formation of a chemical reaction between T2T and BRL.

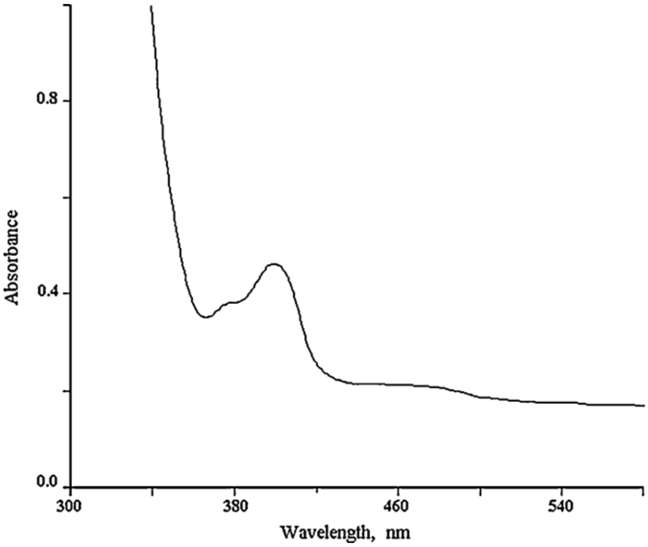


**Fig. 2.** Electronic absorption spectra of the $CH_2Cl_2$ solution of the synthesized solid product (T–B) at 25 °C.

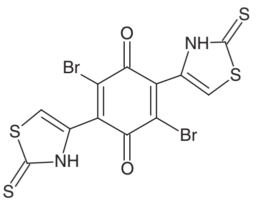
T2T is an electron donor [17,18] and BRL is a well known π-acceptor having 2.44 eV electron affinity [24]. This means that formation of a T2T–BRL CT complex might be probably occurred at least initially [17,18,24,25] when the two species (T2T and BRL) undergo interaction. Several attempts of the spectral measurements by using different concentrations of each of the interacting species have been done to observe a CT spectral band, but failed. However, failure of observing the, expected, CT absorption band(s) for this T2T–BRL interaction in solutions might be due to either the perturbation of this (expected) CT band with the absorptions of the free donor and/or the free acceptor or the existence of the compound T2T in the form of dimeric hydrogen bonded complex in the solid state, whereas dissociation of this complex into its free (interacting) molecules (either in the thione or thiol forms) may require some energy and/or elapsing of time.

### 3.2. Characterization of the product resulted from the interaction of T2T with BRL

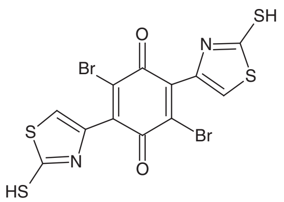
TLC measurements of the synthesized compound (T–B) have shown a single peak which means that the interaction of T2T with BRL has produced a single compound.

The electronic absorption spectra of the $CH_2Cl_2$ solution of the solid product (T–B) have shown a main spectral band located at 400 nm, cf. Fig. 2. This spectral band does not belong to either the individual reacting species: T2T or BRL. In turn, one can suggest that the interaction of T2T with BRL has led to a new compound (T–B) having different electronic transitions rather than those of each individual reacting species.

As shown hereafter, all the data which have been collected from the IR, $^1$H NMR and Mass spectra have indicated that a substitution reaction between T2T and BRL has been occurred. This substitution reaction has been occurred in which two molecules of T2T have been reacted with one molecule of BRL. Also, our available data gathered from all the applied analysis tools (IR, NMR and Mass spectra) have indicated that the product of this chemical reaction (T–B) has the following two structures (Structures V and VI) existing together; i.e. coexistence of both the structural forms: thione and thiol, Structures V and VI, respectively.



Structure V
(thione structure)



Structure VI
(thiol structure)

The IR spectra of the free donor T2T, the free acceptor BRL and the solid product (T–B) synthesized from the interaction of T2T with BRL have been measured, cf. Fig. 3.

A careful examination of the IR spectral data has indicated the coexistence of these suggested structures (Structures V and VI) for the compound T–B. The IR spectra of the synthesized T–B solid compound (cf. Fig. 3) have indicated the existence of the bromanil (in its quinone form), the thione oxidized form of T2T and the thiol oxidized form of the T2T. Thus, the IR spectra of the compound T–B have showed several peaks located at 1715 and 1415 cm$^{-1}$ which characterize [26] to the stretching vibrations of C=O and C=C groups, respectively, for the bromanil (in the two Structures V and VI), cf. Fig. 3. Also, the IR spectra of the compound T–B have showed peaks located at 3200(w) and 1040 cm$^{-1}$ which are characteristic [26] to the groups NH and C=S, respectively, for the thione form (Structure V). Further, the same IR spectra of this compound (T–B) have showed peaks at 2750 and 1590(s) cm$^{-1}$ which are characteristic [26] to the stretching vibrations of SH and C=N groups, respectively, of the thiol form (Structure IV). Meanwhile, the IR spectra of the synthesized solid product (cf. Fig. 3) do not show peak(s) in the range of 3200–3600 cm$^{-1}$ which may characterize [26] to OH group. This confirms that BRL exists in the quinone form and it does not exist in the corresponding hydroquinone (BRLH$_2$).

The $^1$H NMR spectra have provided further evidences for the aforementioned structural formulae (Structures V and VI) of the compound T–B resulted from the interaction of T2T with BRL. The NMR spectra have indicated the coexistence of the previously two suggested structures (Structures V and VI) for the compound T–B.

Thus, the $^1$H NMR spectra (200 MHz, in DMSO) of the solid product (T–B) (cf. Fig. 4) have displayed distinct signals characterizing [26] to the suggested structures (Structure V and VI) namely: $\delta$ (ppm); 8.24 (H, s, 2H of C5 and C19, for the structures V and VI), 7.76 and 7.54 (H, s, 2NH, for the thione structure (St. V)) and 4.08 and 3.82 (H, s, 2SH, for the thiol structure (St. VI)). Moreover, the same $^1$H NMR spectra of the compound T–B (cf. Fig. 4) have provided a set of additional evidences for the formation of the compound T–B, as a product of the chemical reaction between T2T and BRL, and, also, evidences for the coexistence of the aforementioned two suggested structural formulae (Structures V and VI) of this compound. These set of evidences can be manifested in what follows: (1) no signal(s) characterizing [26] to a proton of a phenolic OH group has been shown in these $^1$H NMR spectra (cf. Fig. 4) which means that the primary interacting bromanil (BRL) did not fully reduced to the corresponding hydroquinone. (2) No multiplet signals characterizing [26] to protons of the aliphatic –CH$_2$–CH$_2$– group have been shown in these $^1$H NMR spectra (cf. Fig. 4) which means that each of the primary interacting T2T compound has lost 3 H atoms in the form of H$_2$ and HBr molecules. Thus, in addition to the replacement reaction, which produced HBr molecules, a dehydrogenation by the bromanil via a redox reaction has been occurred too. The –CH$_2$–CH$_2$– group does no longer exist in any form of the final product (T–B). (3) The observation of a singlet signal (at 8.24 ppm) in the NMR spectra of the compound T–B (cf. Fig. 4) indicates that the sites involved in the thione–thiol tautomerization are far from the protons in the positions 5 and 19, and, in turn, existence of the product T–B in either of the two forms (Structures V and VI) do not affect on the resonance (signal position) of the protons in the 5 and 19 positions. This truly confirms that position number 4 of the compound T2T is the active site by which T2T has been reacted with BRL via the replacement reaction. Finally, (4) resonance of the protons in the positions 5 and 19 of the compound T–B (in either of the two forms) have been appeared in the NMR spectra as a singlet sharp signal with high integration, cf. Fig. 4. This confirms that the protons in the positions 5 and 19 are identical having a symmetrical atom-to-atom relationship. Moreover, the coexistence of the two forms (Structures V and VI) has increased and multiplied the integration of the signal of the protons in the positions 5 and 19.

A convincing evidence for the structure of the synthesized compound (Structures V and/or VI) has been attained by examining the Mass spectra of this solid product (T–B) resulting from the interaction of T2T with BRL. Before discussing the Mass spectra, it is worthy to mention that both structures V and VI might have the same spectral peaks; they have the same molecular weight and except for the sites of the tautomerization (the exocyclic S and the endocyclic N atoms) the two structures have the same atom-to-atom relationship. Hence, existence of the product (T–B) in either the two forms (Structures V and VI) or even the coexistence of the two structures does not dramatically affect the Mass spectra (peaks positions and the corresponding fragments).

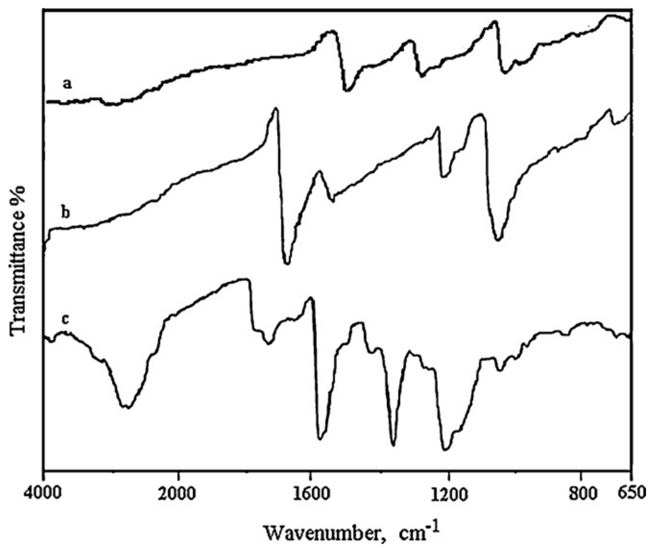


**Fig. 3.** Infrared spectra of: (a) free T2T, (b) free BRL, and (c) T–B (solid product of the T2T–BRL interaction).

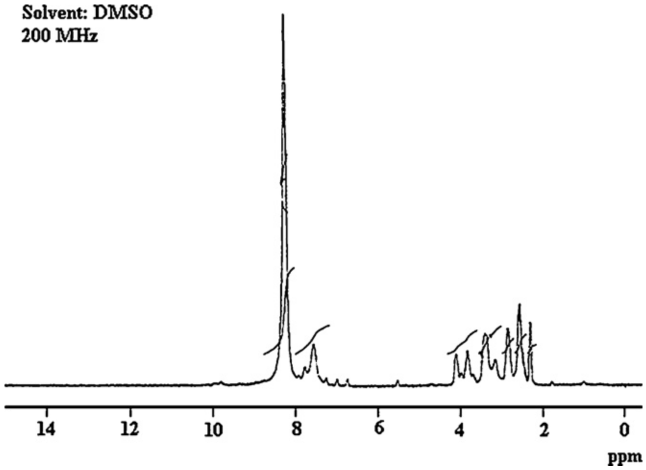


**Fig. 4.** $^1$H NMR spectra of the compound T–B.

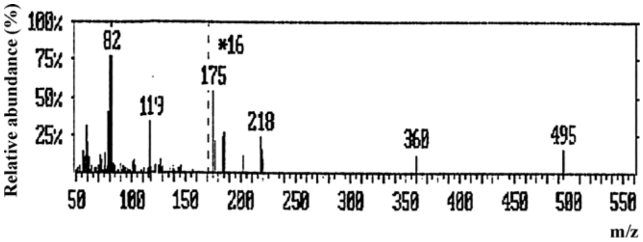


**Fig. 5.** Mass spectra of the compound T–B.

The Mass spectra of the product (T–B) resulted from the interaction of T2T with BRL (cf. Fig. 5) have displayed a peak M (M+1) at $m/z$ (%) = 495 (0.9) suggesting the molecular weight of the assigned product (Structure V or VI) in which the compound T2T has been first oxidized by dehydrogenation to the form T2T-2*H*, whereas two of the oxidized T2T molecules (T2T-2*H*) have been added to a molecule of BRL via a substitution reaction accompanied by the elimination of two HBr groups (Structure V or VI; M.W. = 494). Indeed, this confirms the assigned structures (Structure V or VI) for the compound T–B resulted from the interaction of T2T with BRL.

Thus, one can suggest that the interaction between T2T and BRL has been occurred according to the following steps or reaction pathway: a first formation of an outer sphere CT complex is proposed to be occurred followed by a formation of an inner sphere CT complex [17,18,24,25]. Then a substitution reaction has been occurred between the two interacting species in which two HBr groups have been eliminated. At the same time, dehydrogenation (oxidation) of each of the T2T molecules has been occurred by the aid of other BRL molecules.

We are not yet in a position to prove unambiguously that our suggested reaction pathway is a representative mechanism for the T2T–BRL interaction. However, the structure of the compound resulted from this T2T–BRL interaction via first formation of charge transfer interaction followed by a substitution reaction has found an adequate explanation by the hypothetic reaction pathway. Meanwhile, we believe that further investigations involving X-ray measurements are necessary to complete the study of these amazing interactions of thiazolidine-2-thione (T2T).

## 4. Conclusion

The interaction of T2T with BRL has led to a chemical reaction after an initial formation of a charge transfer complexation, meanwhile the interacting donor (T2T) has been oxidized to the corresponding thiazole. Unexpectedly, and interestingly too, neither the SH group of the thiol form nor the NH group of the thione form of the T2T has shared in the substitution reaction with BRL.

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.saa.2011.10.032.

## References

[1] A.R. Fakhari, S.S. Hosseiny Davarani, H. Ahmar, S. Makarem, J. Appl. Electrochem. 38 (2008) 1743–1747.
[2] D. Nematollahi, E. Tammari, J. Org. Chem. 70 (2005) 7769–7772.
[3] C. Laurence, M.J. El Ghmari, J.Y. Le Questel, M. Berthelot, R. Mokhlisse, J. Chem. Soc., Perkin Trans. 2 (1998) 1545–1551.
[4] J. Leclere, J. Orgiazzi, B. Rousser, J.L. Schlienger, J.L. Wemeau, La thyroïde, Expansion Scientifique Française, Paris, 1992.
[5] J.C. Thomes, F. Comby, J.F. Lagorce, J. Buxeraud, C. Raby, Jpn. J. Pharmacol. 58 (1992) 201–207.
[6] H. Engler, A. Taurog, T. Nakashima, Biochem. Pharmacol. 31 (1982) 3801–3806.
[7] A. Taurog, Endocrinology 98 (1976) 1031–1046.
[8] G.T. Zitouni, S. Sezgin, Acta Pharm. Turc. 40 (1998) 151–154.
[9] D.A. Mc Ginty, W.G. Bywater, J. Pharmacol. 84 (1945) 342;
D.A. Mc Ginty, W.G. Bywater, J. Pharmacol. 85 (1946) 129–139.
[10] O. Gawron, L. Keil, Arch. Biochem. Biophys. 89 (1960) 293–295.
[11] G.R. Handrick, E.R. Atkinson, F.E. Granchelli, R.J. Bruni, J. Med. Chem. 8 (1965) 762–766.
[12] H.S. Mahal, T. Mukherjee, Radiat. Phys. Chem. 54 (1999) 29–37.
[13] C.L. Fang, General Concepts of Additives in the Electroplating Solution, Finishing Science Publication, Taipei, Taiwan, 1996.
[14] L.H. Little, R.H. Ottewill, Can. J. Chem. 40 (1962) 2110–2121.
[15] R. Solmaz, G. Kardas, M. Culha, B. Yazici, M. Erbil, Electrochim. Acta 53 (2008) 5941–5952.
[16] N.L.D. Filho, D.R. do Carmo, F. Gessner, A.H. Rosa, Anal. Sci. 21 (2005) 1309–1316.
[17] U.M. Rabie, M.H.M. Abou-El-Wafa, H. Nassar, Spectrochim. Acta A 78 (2011) 512–517.
[18] U.M. Rabie, M.H.M. Abou-El-Wafa, H. Nassar, Spectrochim. Acta A 79 (2011) 1411–1417.
[19] U.M. Rabie, M.H.M. Abou-El-Wafa, R.A. Mohamed, J. Mol. Struct. 871 (2007) 6–13.
[20] U.M. Rabie, Collect. Czech. Chem. Commun. 71 (2006) 1359–1370.
[21] U.M. Rabie, H.M.A. Salman, M.H.M. Abou-El-Wafa, Bull. Chem. Soc. Jpn. 77 (2004) 681–686.
[22] H.M.A. Salman, M.R. Mahmoud, M.H.M. Abou-El-Wafa, U.M. Rabie, R.H. Crabtree, Inorg. Chem. Commun. 7 (2004) 1209–1212.
[23] H.M.A. Salman, U.M. Rabie, E.M. Abd-Alla, Can. J. Anal. Sci. Spectrosc. 49 (2004) 1–7.
[24] D.R. Lide, Handbook of Chemistry and Physics, 77th ed., CRC Press, 1996–1997.
[25] P. Muller, D. Joly, Helv. Chim. Acta 66 (1983) 1110–1118.
[26] J.B. Lambert, H.F. Shurvell, D.A. Lightner, R.G. Cooks, Introduction to Organic Spectroscopy, Macmillan Publishing Company, New York, 1987.