ΔH = heat of vaporization, cal/mol
M = molecular weight
n = integer constant, Equation 2
P = pressure
q^{st} = isosteric heat of adsorption, cal/mol
q_θ = differential heat of adsorption at constant coverage, cal/mol
R = gas constant, 1.987 cal/mol/K
T = temperature, K
v = liquid molar volume, ml/mol
W = pore volume of adsorbent, ml/g-adsorbent, Equation 1
W° = total pore volume, ml/g-adsorbent

Greek Letters

β = affinity coefficient, E/E_0
ρ^* = adsorbed phase density, g/ml
ρ = liquid density, g/ml
θ = adsorption ratio

Subscripts

o = standard substance
b = normal boiling point
c = critical point
s = saturated state

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NEW COMPOUND SECTION

Synthesis of Benzo[a][1,4]benzothiazino[3,2-c]-phenothiazines and 5H-Benzo[a]phenothiazin-5-ones

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A number of substituted benzo[a][1,4]benzothiazino[3,2-c]-phenothiazines and 5H-benzo[a]phenothiazin-5-ones are synthesized by the condensation reaction of 2,3-dichloro-1,4-naphthoquinone with substituted 2-aminothiophenols and their zinc salts, respectively. The lowering of C═O frequency in 5H-benzo[a]phenothiazin-5-ones is attributed to the ionic resonance effect.

The biological and industrial applications of phenothiazines and their derivatives have led to our interest in the synthesis of nuclear-substituted benzo[a]phenothiazines and their derivatives.

Van Allan and Reynolds (*10*), Akatsuka and Yoshinaga (*1*), and Reynolds et al. (*7*) have reported the synthesis of benzo[a][1,4]benzothiazino[3,2-c]-phenothiazine by the condensation of 2-aminothiophenol (ATPh) with 2,3-dichloro-1,4-naphthoquinone (I) and *N*-(1,4-dioxo-2-methoxynaphthyl-3)-pyridinium methosulfate. This reaction has been extended to a number of substituted 2-aminothiophenols (SATPH). It is quite interesting and surprising that under similar conditions the zinc salt of ATPh and I gave a different compound, i.e., 6-chloro-5H-benzo[a]phenothiazin-5-one. This unusual reaction seemed worthy of further investigation. 2-Amino-5-methoxy and ethoxy thiophenols were synthesized by a slightly modified method as reported earlier (*3–5*). The infrared data are also reported.

Experimental

Ir spectra were recorded for KBr discs with a Beckman IR-4 spectrophotometer. 2-Amino-5-chloro- (*5*), 2-amino-5-bromo- (*5*), 2-amino-5-methyl- (*5*), 2-amino-5-fluoro- (*6*), 2-amino-3-bromo-5-methyl- (*9*), and 2-amino-3,5-dimethyl-benzenethiols (*9*) were prepared by the methods reported earlier. The purity of compounds was checked by tlc on silica gel G (Merck) in various nonaqueous solvent systems. All melting points are uncorrected.

5-Substituted (methoxy or ethoxy)-2-aminobenzenethiols. The hydrolysis of 2-amino-6-methoxy or ethoxy benzothiazoles (0.1 mole) was carried out with a small amount of potassium hydroxide (0.76 mole, 30% solution). This resulted in better yields (*5*) of 2-amino-5-methoxy or ethoxy benzenethiols. 2-Amino-5-methoxy-benzenethiol, yield 52%; mp 104°. 2-Amino-5-ethoxy-benzenethiol, yield 50%; mp 103°.

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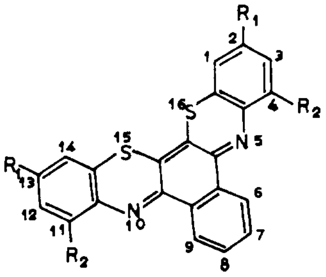
Table I. Substituted Benzo[a][1,4]benzothiazino[3,2-c]-phenothiazines



			Solvent of			ν_{max}, cm^{-1}[b]			
R_1	R_2	Mp, °C	recrystallization	Yield, %	Formula[a]	a	b	c	d
H	H	291	o-Dichlorobenzene	70	$C_{22}H_{12}N_2S_2$	3050			750
Cl	H	>300	Benzene	64	$C_{22}H_{10}Cl_2N_2S_2$	3100	862	823	775
Br	H	>300	Chlorobenzene	57	$C_{22}H_{10}Br_2N_2S_2$	3100	860	822	775
F	H	>300	Benzene	65	$C_{22}H_{10}F_2N_2S_2$	3100	853	820	773
CH_3	H	289	Chlorobenzene	68	$C_{24}H_{16}N_2S_2$	3100	862	821	775
OCH_3	H	208	Benzene–alcohol	77	$C_{24}H_{16}N_2O_2S_2$	3100	854	825	774
OC_2H_5	H	277	o-Dichlorobenzene	79	$C_{26}H_{20}N_2O_2S_2$	3100	852	830	770
CH_3	Br	>300	Trichlorobenzene	57	$C_{24}H_{14}Br_2N_2S_2$	3100	868		773
CH_3	CH_3	>300	Toluene	80	$C_{26}H_{20}N_2S_2$	3100	865		775

[a] Satisfactory C, H, and N analyses have been obtained in all cases. [b] a, aromatic C—H stretching; b, an isolated ring hydrogen atom; c, 1,2,4-trisubstitution; d, 1,2-disubstitution.

Substituted 5H-benzo[a]phenothiazin-5-ones. A mixture of the 2,3-dichloro-1,4-naphthoquinone (0.01 mole) and zinc thiolate of SATPh (0.005 and 0.0125 mole) in dry ethanol (100 ml) was stirred for 1 hr at room temperature. The color of the solution in most cases changed to orange-red; then, the contents were refluxed for 2 hr. The solid which formed on cooling was filtered and washed with 5% hydrochloric acid (ca. 500 ml) and water. Analytical samples were obtained by recrystallizing (three times) with suitable solvents (Table II).

Other reaction solvents such as methanol, toluene, 1,2,3-trichloropropane gave the desired product, but the yields were lower.

Substituted benzo[a][1,4]benzothiazino[3,2-c]-phenothiazines. *Method A.* A mixture of 2,3-dichloro-1,4-naphthoquinone (0.01 mole) and SATPh (0.01 and 0.025 mole) in dry pyridine (50 ml) was stirred for half an hour at room temperature and then refluxed for 2 hr. An equal volume of methanol was added, and the mixture was chilled, filtered, and washed with methanol and water to give the desired product. Analytical samples were obtained by recrystallizing (three times) with suitable solvents. The melting points and other data are summarized in Table I.

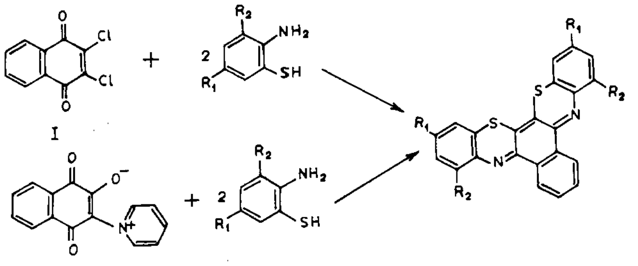
Other reaction solvents such as ethanol, ethoxyethanol, toluene, dimethylformamide, and 1,2,3-trichloropropane gave the same product, but the yields were lower than that in pyridine.

Method B. A mixture of the 1,4-dioxo-3-pyridinium-2-naphthoxide (0.01 mole) and SATPh (0.025 mole) in dry pyridine (100 ml) was refluxed for 2 hr; then, an equal volume of methanol was added, and the mixture was chilled, filtered, and washed with methanol to give the desired product.

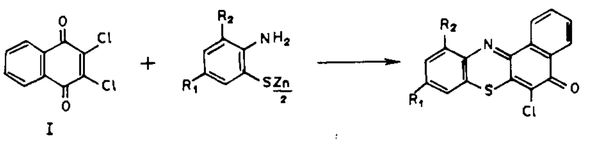
Method C. A mixture of 2,3-dichloro-1,4-naphthoquinone (0.01 mole) and zinc thiolate of SATPh (0.0125 mole) in dry pyridine or dimethylformamide (100 ml) was refluxed for 3 hr, and the mixture was chilled, filtered, and washed with methanol to give the desired product.

Results

Under many reaction conditions, I (0.01 mole) was condensed with SATPh (0.01 and 0.025 mole) in various solvents, i.e., ethoxyethanol, ethanol, toluene, 1,2,3-trichloropropane, dimethylformamide, and pyridine, to give only substituted benzo[a][1,4]benzothiazino[3,2-c]-phenothiazines. These substituted benzo[a][1,4]benzothiazino-[3.2-c]-phenothiazines were also obtained by the reaction 1,4-dioxo-3-pyridinium-2-naphthoxide with SATPh.



When I (0.01 mole) was condensed with zinc thiolates of the same thiophenols (0.005 and 0.0125 mole) in alcohol, toluene, 1,2,3-trichloropropane, and methanol, the substituted 5H-benzo[a]phenothiazin-5-ones were obtained, but in pyridine and dimethylformamide, the zinc thiolates of SATPh and I gave the same product, i.e., substituted benzo[a][1,4]benzothiazino[3,2-c]-phenothiazines.



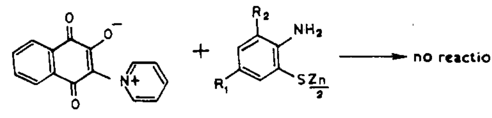
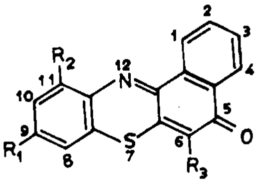


Table II. Substituted 5H-Benzo[a]phenothiazin-5-ones



				Solvent of recrystallization	Yield,		V_{max}, cm^{-1b}					
R_1	R_2	R_3	Mp, °C		%	Formula[a]	A	B	C	D	E	F
H	H	Cl	232[c]	Benzene	84	$C_{16}H_8ClNOS$	3040	1645	1520	1299		760
Cl	H	Cl	282	Benzene	82	$C_{16}H_7Cl_2NOS$	3050	1645	1520	1304	815	770
Br	H	Cl	274	Benzene	80	$C_{16}H_7BrClNOS$	3050	1645	1520	1305	825	775
F	H	Cl	277	Toluene	81	$C_{16}H_7ClFNOS$	3050	1645	1520	1300	822	774
CH_3	H	Cl	242	Toluene	87	$C_{17}H_{10}ClNOS$	3100	1645	1520	1300	820	745
OCH_3	H	Cl	298	Acetone	75	$C_{17}H_{10}ClNO_2S$	3050	1645	1520	1295	820	775
OC_2H_5	H	Cl	292	Chloroform	77	$C_{18}H_{12}ClNO_2S$	3100	1645	1520	1300	825	775
CH_3	Br	Cl	262–265 dec.	Benzene	70	$C_{17}H_9BrClNOS$	3050	1645	1520	1300		775
CH_3	CH_3	Cl	254	Toluene	83	$C_{18}H_{12}ClNOS$	3050	1645	1520	1305		770

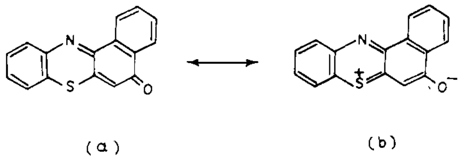
[a] Satisfactory C, H, and N analyses have been obtained in all cases. [b] A, aromatic C—H stretching; B, C═O stretching; C, C═N stretching; D, Ph—N stretching vibration in tertiary amine; E, 1,2,4-trisubstitution; F, 1,2-disubstitution. [c] Lit. (*1*), 225°.

It appears that SATPh have additional driving forces which enhance the reaction to form benzo[a][1,4]benzothiazino[3,2-c]-phenothiazines. The reaction appears to occur via Michael addition, mercaptide ion adding twice to the quinone system, with the elimination of hydrogen chloride and subsequent ring closure through the amino groups.

The zinc salts of SATPh with I gave only substituted 5H-benzo[a]phenothiazin-5-ones. In this reaction, zinc thiolate adds once to the quinone system with the subsequent loss of water and $ZnCl_2$. It appears that the $ZnCl_2$ generated may inhibit further condensation by complexation with the product, but the presence of dimethylformamide or pyridine may neutralize the effect caused by $ZnCl_2$. Additional evidence for this fact is that the thiolates do not react when condensed with 1,4-dioxo-3-pyridinium-2-napthoxide.

Infrared Spectra

The C═O band in phenothiazones (Table II, column B) is at a frequency 30 cm^{-1} lower, than the carbonyl frequency in 1,4-naphthoquinone (*2*). It appears that the sulfur atom at the *β*-position with respect to carbonyl group, has a strong electron donating effect; thus, the ionic-resonance form (b) may contribute appreciably to the ground state.



(a) (b)

Because of this ionic-resonance effect, the C═O bond length increases and thus reduces the carbonyl frequency. Similar effects have been observed in 4-thiapyrones (*8*). The other major bands are also listed in Table II.

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