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Novel Heterocyclics from 3- Substituted-5H-1,2,4-Triazino-[5, 6- *b*]indoles and π-Acceptors

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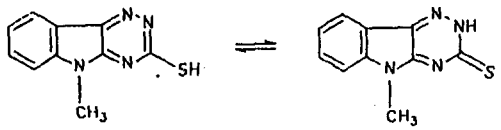
Abstract: The reaction of 1,2,4-triazino[5,6-*b*]indole-3-thione 1 with tetracyanoethylene (TCNE) afforded the disulfide 6, the tricyanovinylation product 8 and thiazolotriazinoindole 11. 3-Aryl-5H-1,2,4-triazino[5,6-*b*] indoles 2a,b reacted with TCNE to give pentacyanopropene 12 and 3-aminotriazinoindole derivatives 14a,b. 3-Hydrazino-5H-1,2,4-triazino[5,6-*b*]indole 3 reacted with TCNE, dicyanomethyleneindane-1,3-dione(CNIND)and 2,3-dicyano-1,4-naphthoquinone(DCNQ)to form triazolotriazinoindoles 17 and the triazepinotriazinoindoles 16,24 and 26. The reaction of 3 with chlorinated quinones gave the quinazolinetriones 21-23.

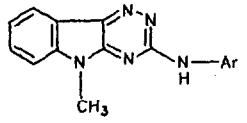
Our long-term continuing interest in chemical reactions induced by charge- transfer (CT) complexation for ms a part of our systematic efforts to obtain new heterocyclic systems. We have earlier investigated. the behaviour of N-arylisoindolines[1,2], arylazoaminopyrazoles[3-5], triazolethiones[6] and aminoparacyclophanes[7] towards π-acceptors to synthesize several new heterocyclic systems and to shed some light on the transannular interactions in paracyclophanes. As a continuation of this work, we have turned our attention to 1,2,4-triazino[5,6-*b*]indole derivatives 1-3 (Fig. 1) as electron donors towards different electron acceptors.

The importance of indole nucleus is well established in the field of pharmaceutical chemistry and in the plant and animal biochemistry[8,9]. The triazino[5,6-*b*]indole derivatives 1-3 (Fig. 1) were reported to possess antiviral, analgesic and hypertensive properties[10-14], and have been utilized for the synthesis of several fused heterocycles[15-24].

Upon adding acetonitrile solutions of TCNE to the solution of thione 1 in acetonitrile a green colour was observed, which quickly changed to blue and which may be attributed to the formation of an unstable CT- complex. (Scheme 1).The unstable CT-complex between 1 and TCNE is followed by electron transfer from donor to TCNE to from TCNE anion radical ($TCNE^{\cdot -}$) 5 in contact with triazinoindole cation radical 4. The recombination of the triazinoindole cation radical 4 in presence of $TCNEH^{\cdot}$ (7) afforded the disulfide 6, as one of the isolated products. The reaction between 6 and 7 gave 8 (λ_{max} =562 nm).On the other hand, the transfer of a proton from the cation radical 4 to $TCNE^{\cdot -}$ 5 generate a sulfur radical 9 within a pair together with $TCNH^{\cdot}$, 7. These two radicals may combine with elimination of a molecule of HCN to afford the tricyanovinylation 10. The latter abstracts a hydrogen molecule from 1 to form the thiazolotriazinoindole 11 after elimination of an another molecule of HCN.



1



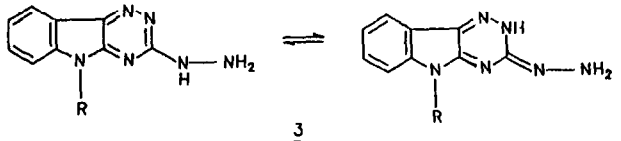
2

a, Ar= C_6H_5

b, Ar= C_6H_4—p—CH_3

c, Ar= C_6H_4—p—OCH_3

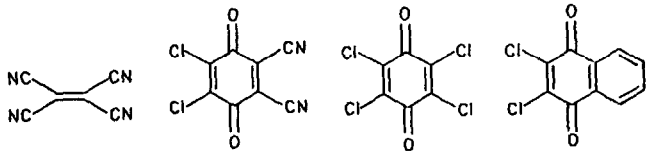
d, Ar= C_6H_4—p—Cl



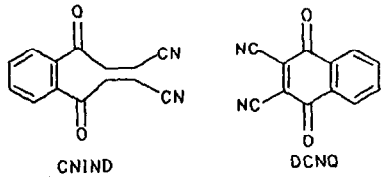
3

a, R= H

b, R= CH_3

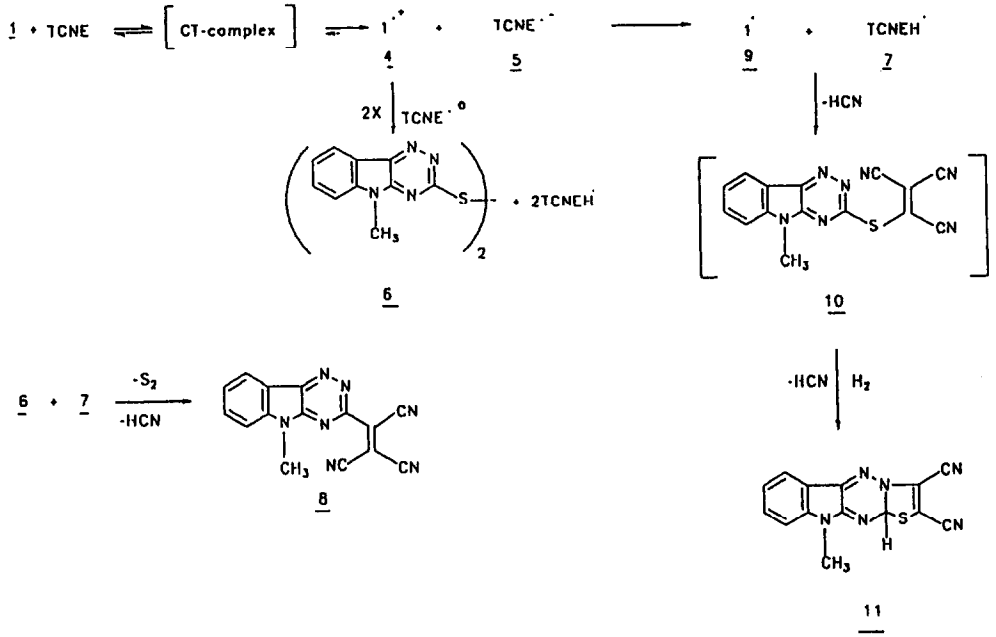


TCNE DDQ CHL DCHNQ



CNIND DCNQ

Fig. 1



Scheme 1

Figure 2 describes the utility of DDQ as dehydrogenating agent[25,26] for 1, a reaction which provides the disulfide 6 and hydroquinone DDQ - H_2.

Fusion of 1 with aromatic amines leads to formation of 3- aryl-5- methyl- 5H-1,2,4- triazino [*5,6-b*] indoles 2. In contrast to 1, interaction of 2 with TCNE afforded pentacyanopropene 12 and 3-N-aryl-N-pyrrolonyl-aminotriazinoindoles 14a,b as illustrated in Scheme 2(λ_{max} for 14a=560 nm and 568 nm for 14b).

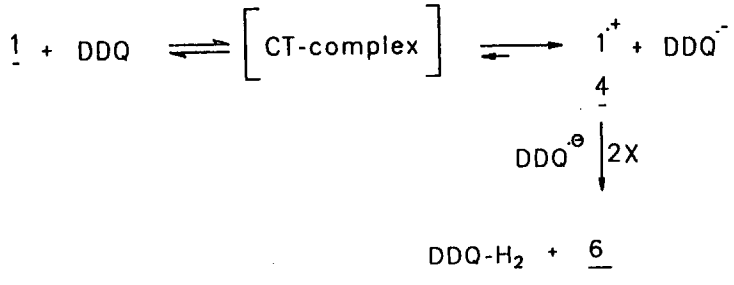
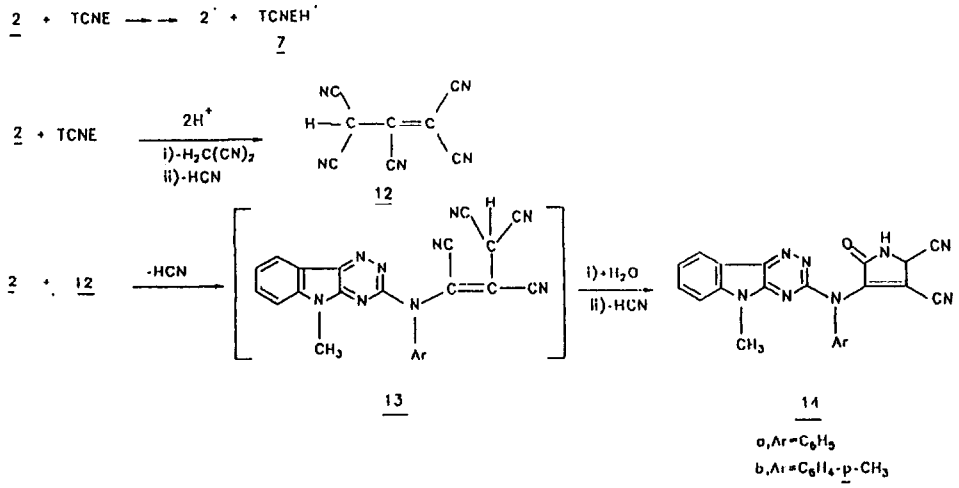


Fig. 2



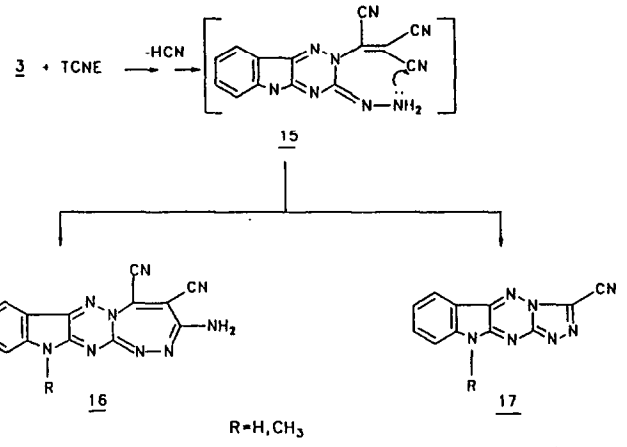
Scheme 2

The structural proof of 14 is based on spectral (Table 1) and analytical data (Table 2). The ^{1}H-NMR spectra clearly indicate the absence of the NH proton attached to the aryl group, and showed a broad singlet at δ=11.90 ,due to NH pyrrole ring. The IR spectra indicated the presence of carbonyl group at 1683 cm^{-1}. The molecular formulae of 14a,b are evidenced from elemental analysis as well as mass spectra. The structure of pentacyanopropene 12 was assigned on the bases of its spectroscopic properties and comparison of its melting point with that reported in the literature[27].

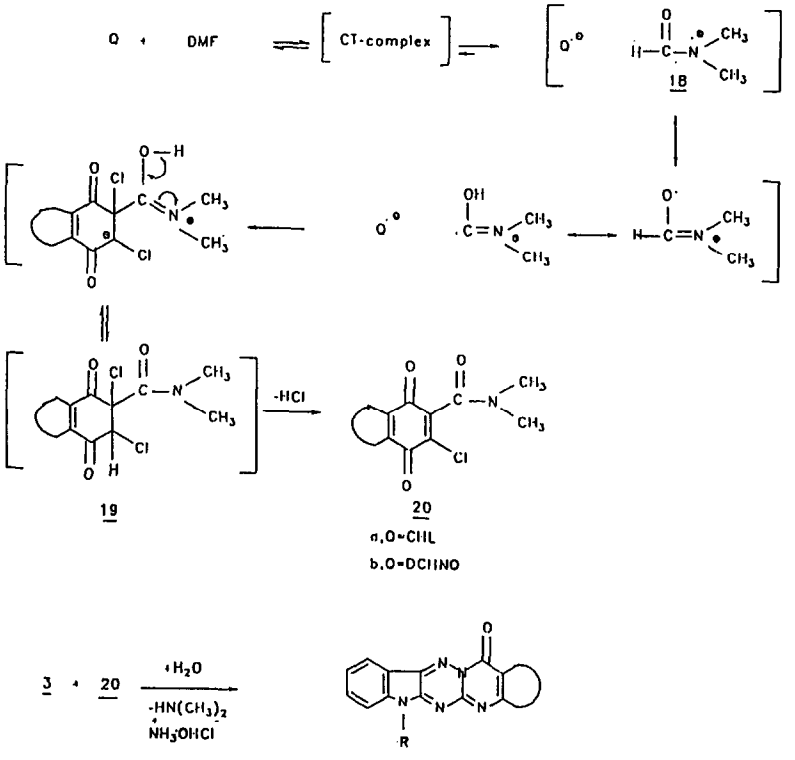
The participation of moist air in the formation of compound 14 as illustrated in the proposed mechanism in Scheme 2 was confirmed by adding donor 2 to TCNE under nitrogen and dry conditions, only a stable CT-complex was formed which dissociates into its components after time and do not follow the given reaction sequence.

On the other hand, the interaction of 5- substituted -3- hydrazino -5H-1,2,4-triazino[*5,6-b*]-indoles 3a,b with TCNE in DMF afforded 3-amino-12-substituted -12H-[1,2,4]triazepino[4,3:2,3]-[1,2,4]triazino[*5,6-b*]indole-4,5-dicarbonitrile (16) and 1,2,4-triazolo[4,3: 2,3][1,2,4]triazino[*5,6-b*]-indole-3-carbonitrile (17) (Scheme 3).

In case of utilizing chlorinated benzo- and naphthoquinones as π -acceptors, the interactions with the donors 3a,b in DMF proceeded in an interesting manner, caused by the participation of DMF. The proposed mechanism for the formation of different quinazolinetrione derivatives 21-23 (Scheme 4) may be explained on the basis of complex formation between DMF and chlorinated quinones, which gradually split off a molecule of hydrogen chloride to form the product 20. The latter interacted with the hydrazinotriazinoindole 3 with elimination of a molecule of dimethylamine and hydroxylamine-hydrochloride in presence of a molecule of water (possibly from moist air or from the solvent) to afford the quinazolinetrione derivatives 21-23.

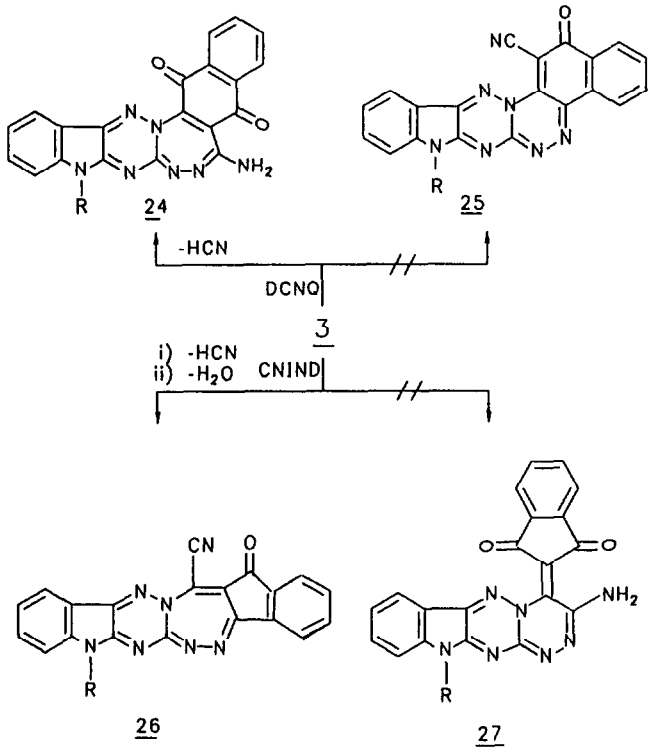


Scheme 3



Scheme 4

The interaction of triazinoindole 3 with CNIND and its facile isomer DCNQ[28] gave oxoindenotriazepinotriazinoindole derivative 26 and napthoquinotriazepinotriazinoindole derivative 24 respectively rather than 27 and 25 (Scheme 5) .The analytical, IR, ^{1}H-NMR, and mass spectral data (Tables 1,2) support the proposed structures 24 and 26. Moreover, it is interesting to show the different behaviour of both CNIND and DCNQ towards the triazinoindole 3.



Scheme 5

Acknowledgement

The authors are deeply indebted to Prof. Dr. H. Hopf, Institute for Organic Chemistry, Braunschweig University for measuring MS and ^{1}H-NMR spectra.

Experimental:

Melting points: are uncorrected. - IR spectra: Shimadzu 470, Nicolet 320 FT-IR, KBr pellets.- ^{1}H-NMR: Bruker WM 400 (400 MHz) using tetramethylsilan (TMS) as the standard and chemical shifts are given on the δ scale .- Mass spectra: Finnigan 8430, 70 eV .-Elemental analysis: Microanalytical Center at Cairo University.

Preparation of layer chromatography

Air dried 1.00 mm layers of silica gel, Merck Pf 254 on plates were employed for preparative TLC and zones were detected by indicator fluorescence quenching exposure to 254 nm U.V. light.

Compounds:

Tetracyanoethylene (TCNE, EGA) was recrystallized from chlorobenzene and sublimed. 2,3-Dicyano-5,6-dichloro-1,4-benzoquinone (DDQ, Aldrich) was recrystallized from benzene /chloroform (2:3). 2,3,5,6,- Tetrachloro-1,4-benzoquinone (chloranil, CHL, Aldrich) was recrystallized several times from benzene before use. Dicyanomethyleneindane-1-3-dione (CNIND) was prepared according to the procedure described by Chatterijee[29] and recrystallized from acetonitrile. 2,3-Dicyano-1,4-naphthoquinone (DCNQ) was prepared from 2,3- dichloro- 1,4- naphthoquinone (DCHNQ, Merck) according to Budni et al[30]. 5-Methyl-5H-1,2,4-triazino [*5,6-b*] indole-3-thione 1, 5-substituted-3-hydrazino-5H-1,2,4-triazino [*5,6-b*] indole 3a,b were prepared according to literature[11,31]. 3-Aryl-5-methyl-5H-1,2,4-triazino [*5,6-b*] indoles 2a,b were prepared in a similar procedure described for the preparation of 3-aryl-5-ethyl-5H-1,2,4-triazino [*5,6-b*] indoles[19]. Acetonitrile, dichloromethane and dimethylformamide (DMF) were used as solvents purified following Voge[32], dried and distilled.

1- Reaction of 5-methyl-5H-1,2,4-triazino [*5,6-b*] indole-3- thione (1) with TCNE

To a stirred solution of 256 mg (0.002 mol) of TCNE in 10 ml of dry acetonitrile the triazinoindole 1 (0.001 mol) in 20 ml. of acetonitrile was added dropwise at room temperature. The colour of the reaction mixture was changed quickly from green to brown and finally to blue. The stirring was continued for 48 hours. The reaction mixture was filtered and the precipitate was washed several times with cold acetonitrile until the mother liquor became colourless. The filtrate was concentrated and the residue was then chromatographed on thin layer plates using toluene/ethyl acetate (4:1) as eluent to give a deep blue zone contained compound 8. The base line of the TLC has been rechromatographed using chloroform/methanol (5:1) as eluent to give a yellowish brown zone contained compound 11. Extraction of the zones with acetone and recrystallization from a suitable solvent afforded the pure compounds (see Table 2) The precipitate was washed several times with cold acetonitrile and recrystallized from DMF to give colourless crystals of the disulfide.6

2- Reaction of 5-methyl-5H-1,2,4-triazino[*5,6-b*] indole-3-thione (1) with DDQ.

To a solution of 227 mg DDQ (0.001 mol) in 15 ml dry acetonitrile, the triazinoindole 1 (0.001 mol) in 20 ml acetonitrile was added dropwise with stirring at room temperature. Thereafter, the mixture was stirred for 12 hours, filtered and the precipitate was washed with cold acetonitrile several times and recrystallized to give a colourless crystals of the disulfide 6. The filtrate was concentrated to yield DDQ-H_2 .

3- Reaction of 3 - aryl-5-methyl-5H-1,2,4-triazino [*5,6-b*] indole 2a,b with TCNE.

To a solution of 256 mg (0.002 mol)TCNE in 15 ml dry dichloromethane, a solution of aryltriazinoindole 2a,b in 30 ml dry dichloromethane was added and stirred at room temperature, and the stirring was continued for 96 hours. The solvent of the reaction was evaporated and the residue was then chromatographed on TLC using toluene/ethyl acetate (1:1) as eluent. The fastest migrating zone contained the pentacyanopropene 12 and the slowest migrating one (which is always characterized by deep blue colour) contained compound 14. Extraction of the zones with acetone gave a residue, which was rechromatographed several times with the same eluent to separate a pure compounds. Recrystallization from a suitable solvent afforded the compounds 14a,b (see Table 2).

4- Reaction of 5-substituted -3-hydrazino-5H-1,2,4-triazino [*5,6-b*] indole 3a,b with TCNE.

A solution of hydrazinotriazinoindoles 3a,b (0.001 mol) in 10 ml DMF was added dropwise to a solution of 256 mg (0.002 mol) of TCNE in 10 ml DMF with stirring at room temperature. The mixture was stirred for 48 hours and the solvent was concentrated. The obtained brown residue was dissolved in methanol and chromatographed on TLC, using toluene/ethyl acetate(2:1) as eluent to give two zones; the first contained compound 16 and the second the triazolotriazinoindole 17. The two zones were extracted with acetone and recrystallized from a suitable solvent to afford the pure compounds (see Table 2)

5- Reaction of 5-substituted-3-hydrazino-5H-1,2,4-triazino [5,b-b]indole 3a,b with DDQ

To a solution of DDQ(0.001 mol)in 15 ml DMF a solution of hydrazinotriazinoindole 3a,b (0.001 mol) in 15 ml. DMF was added and the mixture was stirred for 72 hours. The solvent was concentrated and the crystals of quinazolinetrione derivatives 21 a;b were precipitated which washed with ethanol. Recrystallization from DMF afforded pure compounds (seeTable 2).

6- Reaction of 5-substituted-3-hydrazino-5H-1,2,4-triazino [*5,6-b*]indole 3a,b with CHL.

To a solution of 246 mg CHL(0.001 mol) in 15 ml DMF a solution of 3a,b (0.001 mol) in 15 ml DMF was added with stirring at room temperature ,the colour of the reaction mixture changed gradually from green to blue. The stirring was continued for 72 hours with admission of air to complete the reaction the solvent was evaporated and the residue was dissolved in methanol and chromatographed on TLC using toluene as eluent. The fastest migrating blue zone contained 20a, the base line of the TLC was rechromatographed using toluene / ethyl acetate (1:1) as eluent contained the quinazolinetrione derivatives 23a,b. Extraction of the zones with acetone and recrystallization from a suitable solvent afforded the pure compounds (see Table 2).

Table 1: The ^{1}H - NMR, IR and mass spectra of compounds 2 a-d , , 6, 8, 11, 14 a, b, . 16 a,b ,17a,b, 20 a,b, 21 - 24 and 26 a,b.

Compound	^{*1}H-NMR (δ, TMS)	IR(KBr, cm^{-1})	MS m/z(rel. intensity %)
2a	3.80(s,3H) indole-N-CH_3; 7.10- 8.10 (m,9H)Ar-H; 10.10 (s,1H) NH-Ar	3400-3260 (NH); 3100-3020 (Ar-CH) ;2970 (Ali-CH); 1620-1600, 1580 (Ar-C = C).	275(M^+, 56); 274(100); 247(6); 246(31); 231(7); 149(13); 57(38).
2b	2.35(s,3H) CH_3; 3.81(s,3H) indole-N-CH_3; 7.39-8.14 (m,8H) Ar-H; 10.10 (s,1H) HN-Ar.	3360(NH);3040(Ar-CH); 2900 (Ali-CH); 1620-1600, 1580 (Ar-C = C).	
2c	3.76(s,3H)indole -N-CH_3; 3.87 (s,3H)OCH_3; 7.00-7.86 (m,8H) Ar-H; 10.00 (s,1H)HN-Ar.	3310(NH); 3050, 3100(Ar-CH); 2900-2950 (Ali-CH); 1610, 1590(Ar-C = C).	
2d	3.78(s,3H)indole -N- CH_3; 7.63-8.23(m,8H)Ar-H;10.12 (s,1H) HN-Ar.	3380(NH);3060(Ar-CH); 2980 (Ali-CH);1620-1600,1580 (Ar.C =C).	
6	Insoluble in DMSO or deuterated common solvent.	3050(Ar - CH);2920 (Ali-CH); 1620; 1580 (Ar - C=C)	430 (M^+, 34); 402(17); 344 (9); 215 (100); 187 (41); 143 (47); 77(32).
8	3.70(s,3H)- indole N-CH_3; 7.10-7.60 (m,4H) Ar-H	2921(Ali-CH);2208(CN); 1603 (Ar-C = C).	286 (M^{+1}, 100); 271(25); 260(3); 185 (9); 169(7); 144(20).
11	3.80(s,3H) indole N-CH_3; 5.65 (s,1H)CH-thiazole ring; 7.75-8.40 (m,4H)Ar-H.	2956,2925 (Ali-CH);2210 (CN); 1602,1584 (Ar-C = C).	292(M^+,49);266(100);251(63);219 (35) ;193(32); 91(51).
14a	3.70(s,3H)indole-N-CH_3; 6.50 -8.30 (m,10H)Ar-H and CH-Pyrrole ring; 11.90 (s,br,1H) NH pyrrole ring.	3332,3231,3170(NH);2958,2944 (Ali-CH); 2205(CN); 1683 (CO); 1638,1609,1578 (Ar-C= C).	406(M^+,13);405(38); 248 (100); 57(75).
14b	2.38(s,3H) CH_3; 3.65(s,3H) indole -N-CH_3; 6.76-8.31 (m,9H)Ar-H and CH-pyrrole ring; 11.87 (s,br,1H) NH pyrrole ring.	3381,3343,3216(NH);2937(Ali-CH), 2225, 2208(CN); 1680 (CO);1638, 1587(Ar-C=C).	420 (M^+,7); 419(13); 288 (17);266(34);208(32);136 (67);119(72);91(100); 57 (83).
16a	7.50-8.40(m,4H)Ar-H; 8.65 (s,br,2H)NH_2;9.43(s,br,1H) indole NH.	3420 - 3280(NH_2, NH); 2220 (CN); 1640-1610 (Ar- C = C).	
16b	3.80(s,3H) indole N-CH_3; 7.56- 8.42 (m,4H)Ar-H;8.70 (s1 ,br,2H) NH_2.	3360,3280,3230(NH_2); 2227 (CN); 1640, 1625, 1596 (Ar-C=C).	315(M^+,100); 286(6); 272(9); 185(10); 171(13); 143(15).
17a	7.40-8.40(m,4H)Ar-H; 9.40(s, br, 1H) indole - NH.	3430-3320(NH);3060(Ar-CH); 2220(CN).	
17b	3.80(s,3H)indole N-CH_3; 7.30-8.25 (m,4H) Ar-H.	3084(Ar-CH); 2937(Ali-CH); 2222(CN); 1630, 1591 (Ar-C=C).	250(M^{+1},100), 235(5); 199(7); 184 (9); 170(12); 143(25); 116 (21).

Table 1 continued.

Compund	*^{1}H-NMR(δ,TMS)	IR(KBr,cm^{-1})	MS m/z(rel.intensity%)
20a	3.36-3.44(s,6H)-CON(CH_3)$_2$	2920-2970(Ali-CH);1685 (CO).	281/283(M^+,35);255(82) ; 253(71);167 (50); 149 (100).
20b	3.31-3.40(s,6H)-CON(CH_3)$_2$; 7.72-8.00 (m,4H) Ar-H	2910-2960(Ali-CH); 1675 (CO); 1630, 1590(Ar-C=C).	263/265(M^+,21);235(100) ; 220(69); 206 (20); 200 (24); 76(38).
21a	7.30-7.95(m, 4H)Ar-H; 9.45(s,br,1H)indole-NH.	3410-3380 (NH); 2210(CN); 1710 (CO) , 1640,1600,1580 (Ar-C=C).	
21b	3.76(s, 3H)indole-N-CH_3; 7.40-8.20 (m, 4H)Ar-H.	3089-3060 (Ar-CH); 2210 (CN); 1720 (CO); 1620-1591 (Ar-C=C).	381(M^+,38);366(7);240 (20); 224(25); 200(30); 199(100); 171(75); 156 (63); 143(58).
22a	7.24-8.12 (m,4H)Ar-H; 9.48 (s,br,1H) indole NH.	3420-3310(NH);3070(Ar-CH) ; 1670(CO).	
22b	3.72(s,3H) indole-N-CH_3; 7.34-8.16 (m,4H) Ar-H.	1680(CO); 1620-1600 (Ar-C=C).	400/403 (M^+,56); 385 (22); 349(61); 313(11); 170(100); 142(66); 115 (52).
23a	7.30-8.22 (m,8H) Ar-H; 9.46(s,br,1H) indole-NH.	3405-3369 (NH); 3091-3060 (Ar-CH); 2968 (Ali-CH); 1666(CO);1609,1586(Ar-C=C).	367(M^+,100); 339(56); 313(13); 285 (22); 254 (18); 185(63); 157(44); 103 (36); 76(31).
23b	3.78 (s,3H)indole-N-CH_3; 7.34 - 8.18 (m,8H) Ar-H.	3121-3067 (Ar-CH); 1668 (CO); 1585 (Ar-C = C).	381(M^+,50); 353(100); 326(10); 299 (13); 199 (81); 171(52); 156(48); 143 (42); 102(36)
24a	7.45-7.75 (m,8H) Ar-H; 8.50 (s,br,2H) NH_2; 9.40 (s,br,1H) indole-NH.	3410,3360 (NH,NH_2); 1752 (CO); 1620, 1600, 1590(Ar-C=C).	381(M^+,22); 307(38); 293(81); 170 (100); 142 (50); 115(41); 88(31).
24b	3.82 (s,3H) indole-N-CH_3; 7.52-8.10 (m,8H) Ar-H; 8.45 (s,br,2H) NH_2.	3419-3310 (NH_2); 3056(Ar-CH); 2937 (Ali-CH); 1736 (CO); 1628,1582(Ar-C=C).	395(M^+,25); 393(100); 365(13); 349 (27); 315 (63); 104(19); 76(23).
26a	7.40-8.15 (m,8H) Ar-H; 9.50 (s, br,1H) indole-NH	3449-3260(NH); 3105-3056 (Ar-C = C); 2231 (CN);1670 (CO).	363(M^+,100); 335(81); 307(13); 255 (25); 195 (63).
26b	3.80 (s,3H) indole-N-CH_3; 7.45-8.20 (m,8H) Ar-H.	3069(Ar-CH); 2934(Ali-CH); 2210(CN); 1663(CO); 1638, 1591(Ar-C=C).	377(M^+,100); 349(63); 306(7); 255(9);143(17); 102(19).

* All the compounds measured in DMSO-d_6, except 2b,c and 20a,b in $CDCl_3$.

Table 2: Analytical and physical data of compounds 2a,b,6,8,11,14a,b,16a,b,17a,b,20a,b,21-24 and 26a,b

Compund	Yield %	m.p. °C	Colour of crystal	Solvent of recrystallization	Mol. Formula M. Wt	Analysis % Found (Calcd) C	H	N	S	Cl
2a	77	261-63	Pale yellow	Acetonitrile	$C_{16}H_{13}N_5$ (275.314)	69.62 (69.80	4.88 4.76	25.36 25.44)		
2b	73	257-59	Yellow	Ethanol	$C_{17}H_{15}N_5$ (289.341)	70.76 (70.57	5.44 5.23	24.36 24.21)		
2c	68	231-33	Greenish yellow	Ethanol	$C_{17}H_{15}N_5O$ (305.340)	67.03 (66.87	4.79 4.95	23.11 22.94)		
2d	75	289-91	Yellow	Ethanol	$C_{16}H_{12}N_5Cl$ (309.759)	61.94 (62.04	4.08 3.90	22.49 22.61		11.28 11.45)
6	46	302-04	Colourless	DMF	$C_{20}H_{14}N_8S_2$ (430.519)	55.98 (55.80	3.49 3.28	25.87 26.03	14.78 14.90)	
8	21	329-31	Blue	Ethanol	$C_{15}H_7N_7$ (285.269)	63.24 (63.16	2.59 2.47	34.19 34.37)		
11	28	>350	Yellowish brown	Ethanol	$C_{14}H_8N_6S$ (292.325)	57.21 (57.52	2.87 2.76	28.97 28.75	11.12 10.97)	
14a	48	349-52	Blue	Acetonitrile	$C_{22}H_{14}N_8O$ (406.408)	64.84 (65.02	3.65 3.47	27.33 27.57)		
14b	52	>350	Blue	Acetonitrile	$C_{23}H_{16}N_8O$ (420.435	65.44 (65.71	4.11 3.84	26.82 26.65)		
16a	63	332-34	Buff	DMF	$C_{14}H_7N_9$ (301-272)	56.11 (55.81	2.47 2.34	42.08 41.84)		
16b	58	355-57	Buff	DMF	$C_{15}H_9N_9$ (315.299)	57.31 (57.14	2.69 2.88	40.22 39.98)		
17a	24	259-61	Pale yellow	Ethanol	$C_{11}H_5N_7$ (235.21)	56.07 (56.17	2.33 2.14	41.56 41.69)		
17b	26	273-75	Pale yellow	Ethanol	$C_{12}H_7N_7$ (249.237)	57.75 (57.83	3.06 2.83	39.51 39.34)		

Table 2: continued.

Compund	Yield %	m.p. °C	colour of crystal	Solvent of recrystallization	Mol. Formula M. Wt	Analysis % Found (Calcd) C	H	N	S	Cl
20a	15	103-05	Blue	Pet.ether	$C_9H_6NCl_3O_3$ (282.511)	38.07 (38.26	1.96 2.14	5.12 4.96		37.83 37.65)
20b	12	76-78	Red	Pet-ether	$C_{13}H_{10}NClO_3$ (263.680)	59.39 (59.22	3.76 3.82	5.24 5.31		13.33 13.45)
21a	77	287-89	Brown	Ethanol	$C_{18}H_5N_7O_3$ (367.285)	58.69 (58.86	1.51 1.37	26.62 26.70)		
21b	79	296-97	Brown	Ethanol	$C_{19}H_7N_7O_3$ (381.312)	60.13 (59.85	1.94 1.85	25.58 25.71)		
22a	57	239-41	Yellowish brown	Ethanol	$C_{16}H_5N_5Cl_2O_3$ (386.155)	(49.64 (49.77	1.48 1.31	18.36 18.14		18.23 18.36)
22b	66	273-75	Yellowish brown	Ethanol	$C_{17}H_7N_5Cl_2O_3$ (400.182)	50.87 (51.02	1.91 1.76	17.77 17.50		17.62 17.72)
23a	74	329-31	Red	DMF	$C_{20}H_9N_5O_3$ (367.324)	65.62 (65.40	2.55 2.47	18.86 19.07)		
23b	77	349-51	Red	DMF	$C_{21}H_{11}N_5O_3$ (381.350)	65.89 (66.14	3.14 2.91	18.23 18.37)		
24a	69	264-66	Yellow	Ethanol	$C_{20}H_{11}N_7O_2$ (381.355)	63.14 (62.99	2.76 2.91	25.96 25.71)		
24b	65	296-98	Yellow	Ethanol	$C_{21}H_{13}N_7O_2$ (395.382)	63.66 (63.79	3.42 3.31	24.97 24.80)		
26a	87	265-67	Red	DMF	$C_{20}H_9N_7O$ (363.340)	66.28 (66.11	2.67 2.50	27.18 26.99)		
26b	89	279-81	Red	DMF	$C_{21}H_{11}N_7O$ (377.366)	66.95 (66.84	3.11 2.94	26.14 25.98)		

7- Reaction of 5- substituted -3-hydrazino-5H-1,2,4-triazino [*5,6-b*] indole 3a,b with DCHNQ.

To a solution of DCHNQ (0.001 mol) in 15 ml of DMF, a solution of 3a,b (0.001 mol) in 15 ml DMF was added with stirring for 3 hours, a reddish brown crystals were precipitated. The mixture was filtered and the precipitate was recrystallized from DMF to give a reddish brown crystals of 23a,b. The filtrate was concentrated and chromatographed on TLC using toluene / ethylacetate (10 :1) as eluent to give a red zone contained compound 20b. Extraction of the zone with acetone and recrystallization from a suitable solvent afforded the pure compounds (see Table 2) .

8- Reaction of 5-substituted-3-hydrazino-5H-1,2,4- triazino [*5,6-b*] indole 3a,b with CNIND.

To a stirred solution of 208 mg (0.001 mol) of CNIND in 15 ml DMF, the hydrazinotriazinoindole 3a,b (0.001 mol) in 15 ml DMF was added dropwise at room temperature.The colour of the reaction mixture changed gradually from green to red. After standing for 24 hours a red crystals were precipitated. Recrystallization of the precipitate from DMF gave the pure compounds 26a,b (Table 2).

9- Reaction of 5-substituted-3-hydrazino-5H-1,2,4-triazino [*5,6-b*] indole 3a,b with DCNQ.

To a stirred solution of 208 mg (0.001 mol) DCNQ in 10 ml DMF the hydrazinotriazinoindole 3a,b (0.001 mol) in 15 ml DMF was added at room temperature. The reaction mixture was left for 48 hours and the colour was changed to yellowish brown. The solvent was evaporated and the residue was dissolved in methanol, chromatographed on TLC using toluene/ethyl acetate (1:1) as eluent to afford one zone contained the product 24. Recrystallization from suitable solvent gave a pure compound 24 (Table 2).

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