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SUBSTITUTED 5-T-BUTYL TETRAZOLINYL AND PHOTOTETRAZOLINYL RADICALS

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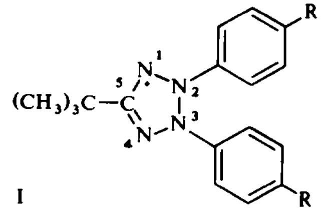
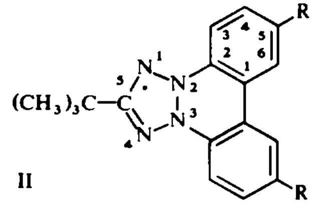
Abstract—A series of tetrazolinyl (I) and phototetrazolinyl (II) radicals with electron donating and electron withdrawing substituents were prepared. The stability of these radicals increases with the electron withdrawing power of the substituents. Ia is the first tetrazolinyl to be isolated. The ESR and UV spectra and the validity of Walter's O, S classification of free radicals are discussed.

THE formation,[1-4] constitution,[5] and spin density distribution[6] of the tetrazolinyls, the free radical intermediates between formazans and tetrazolium salts, have been studied in detail by means of ESR spectroscopy of the free radical solutions. The aim of this investigation was to try to synthesize and to study a series of tetrazolinyls (I) and phototetrazolinyls (II)[7-11] with electron donating and electron accepting substituents, which show the influence of substitution on the stability and on other chemical or physical properties of these radicals. According to their structure, I and II should be radicals of Walter's class O[12] and should exhibit behaviour consistent with the Hammett relationship. Thus donor and acceptor substituents should shift ESR and UV spectra in opposite directions. We chose the series with a t-Bu group in position 5 because the t-Bu group is non-polar, has stabilizing properties by steric shielding, and provides better solubility.



I

	R	m.p. (dec)
Ia	NO_2	126–127°
Ib	CN	--
Ic	$COOCH_3$	--
Id	H	--
Ie	CH_3	--
If	OCH_3	--

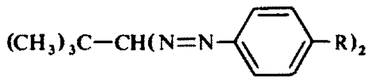


II

	R	m.p.(dec)
IIa	NO_2	--
IIb	CN	289–292°
IIc	$COOCH_3$	254–255°
IId	H	128°
IIe	CH_3	--
IIf	OCH_3	--

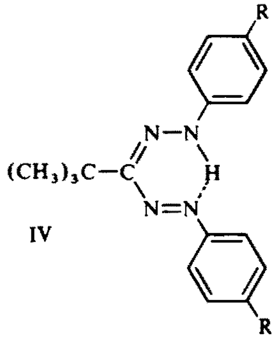
Synthesis of the basic compounds

In contrast to the normal formazan formation,[13] the coupling of diazonium salts with pivaldehyde arylhydrazones in pyridine/dimethylformamide solution yielded stable 1,1-bis(arylazo)neopentanes (III) which had to be isomerized to the red *trans-syn* formazans (IV) by potassium methoxide in dimethylformamide (IIIc–f) or by standing in pyridine solution for 10 hr (IIIa, b).



III

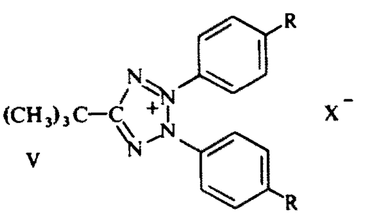
	R	m.p. (dec)
IIIa	NO_2	121–122°
IIIb	CN	134–135°
IIIc	$COOCH_3$	118–120°
IIId	H	103–104°
IIIe	CH_3	62–63°
IIIf	OCH_3	90–91°



IV

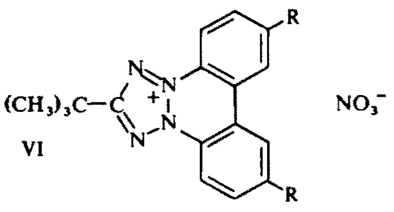
	R	m.p. (dec)
IVa	NO_2	212–213°
IVb	CN	204–205°
IVc	$COOCH_3$	165–166°
IVd	H	70–71°[14]
IVe	CH_3	99–100°
IVf	OCH_3	93–94°

The tetrazolium salts Va–f were obtained by the oxidation of the formazans IVa, b, c and f with N-bromosuccinimide[15] and of IVe with amyl nitrite[16] (to exclude unwanted bromination of the Me groups). The photodehydrogenation of Vb, c, d and e gave the phototetrazolium salts VIb, c, d and e in good yields, sometimes accompanied by substituted benzo[*c*]cinnolines simultaneously formed as photodecomposition products. The photodehydrogenation of Va and Vf failed, even when the tetrazolium nitrates were employed. These findings are in agreement with the observation of Jerchel and Fischer,[9] who were also unsuccessful in getting the comparable phototetrazolium salts from 5-phenyl-2,3-bis(4-nitrophenyl)tetrazolium chloride and 2,3,5-tris(4-methoxyphenyl)tetrazolium nitrate.



V

	R	X^-	m.p. (dec)
Va	NO_2	Br^-	260–261°
Va	NO_2	NO_3^-	232°
Vb	CN	Br^-	276–277°
Vc	$COOCH_3$	Br^-	248–249°
Vd	H	NO_3^-	250°[14]
Ve	CH_3	Cl^-	>300°
Vf	OCH_3	Br^-	234–235°

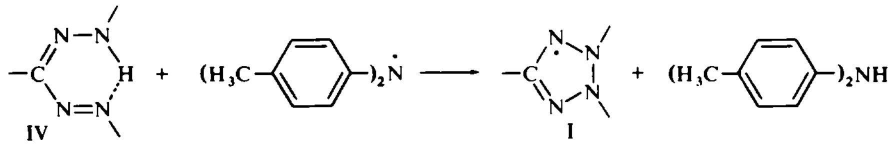


VI

	R	m.p. (dec)
VIb	CN	>300°
VIc	$COOCH_3$	>300°
VId	H	380°[14]
VIe	CH_3	>300°

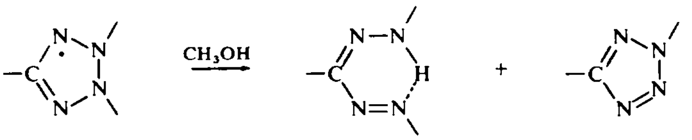
Tetrazolinyl radicals (I)

The tetrazolinyl radicals (Ia–f) were obtained by abstraction of a hydrogen from the formazans (IVa–f) with di-*p*-tolyaminyl[5, 17] in benzene at 40° and were identified through ESR measurements.



The dehydrogenation of the formazan IVa yielded 5-t-butyl-2,3-bis(4-nitrophenyl)-tetrazolinyl (Ia) the first crystallized tetrazolinyl to be isolated, which precipitates from benzene–ligroin as green–black needles, m.p. 126–127° (dec). However, all attempts to isolate other pure crystallized tetrazolinyls from the brownish-green reaction mixtures containing Ib–f failed. The very careful evaporation and investigation of these reaction mixtures resulted only in the isolation of rather impure solid tetrazolinyls (Ib and Ic), reactant formazans and tetrazoles (VII).

The tetrazolinyl Ia is oxidized by bromine to the tetrazolium bromide Va and is easily reduced by sodium dithionite to yield the formazan IVa. In weakly acidic media (e.g. even methanol) Ia immediately decomposes to the formazan IVa and 5-t-butyl-2-(4-nitrophenyl)tetrazole (VIIa). No 3-t-butyl-6-nitro-1,2,4-benzotriazine is formed under these conditions, although it can be readily obtained by dissolving IVa in a mixture of glacial acetic and sulfuric acid.



Ia 54% IVa 27% VIIa

TABLE 1. MAGNETIC DATA ON Ia (χ = MOLAR SUSCEPTIBILITY)

Temp °K	$\chi_{meas} \cdot 10^6$	$\chi_{diamag} \cdot 10^6$ (Pascal)	$\chi_{paramag} \cdot 10^6$	μ_{eff}/μ_B
298°	985	183	1168	1·67
195°	1570	183	1753	1·66
90°	3570	183	3753	1·65

The crystallized tetrazolinyl Ia is monomeric in the solid state and in solution at temperatures down to 90°K. The magnetic moments μ_{eff}/μ_B as measured with a magnetic balance are 1·67 at 298°K, 1·66 at 195°K and 1·65 at 90°K (Table 1, the theoretical value of a monoradical is 1·73). These values correspond to a free radical content of 94%. The UV spectrum of Ia (compared with the UV spectra of the formazan IVa and the tetrazolium salt Va in Fig 1) is characterized by a long wave absorption at 590 mμ (log ε 3·59). The low temperature UV spectrum of Ia in toluene: i-pentane: methylcyclohexane = 1:3:6 shows only slight spectral changes corressponding to the known temperature dependence of electronic spectra. No dimerization or association of the radical occurs at temperatures down to 90°K.

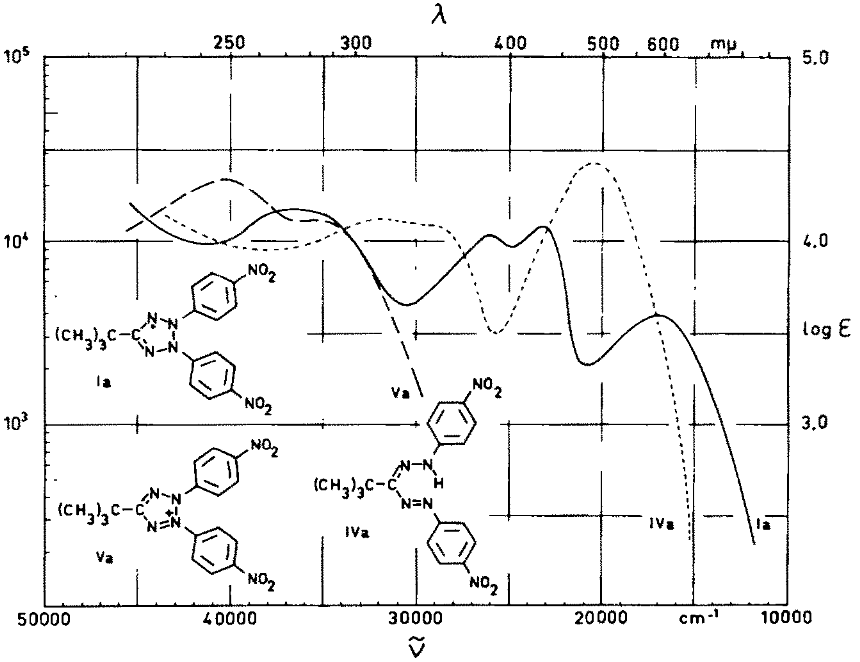


FIG. 1 UV spectra of 5-t-butyl-2,3-bis(4-nitrophenyl)tetrazolinyl (Ia) in dioxane ————, 5-tert-butyl-2,3-bis(4-nitrophenyl)tetrazolium bromide (Va) in ethanol — — —, and 3-tert-butyl-1,5-bis(4-nitrophenyl)formazan (IVa) in dioxane - - - - - - -.

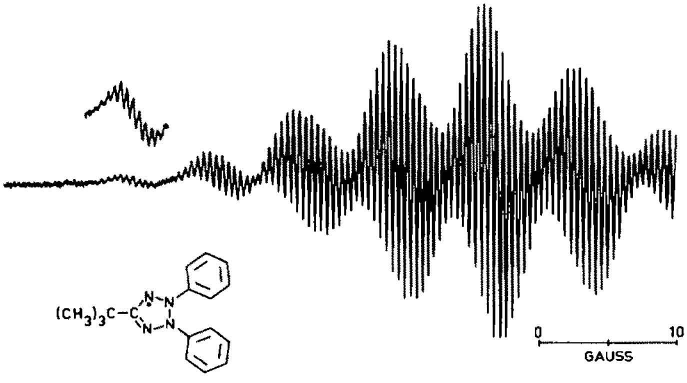


FIG. 2. Slightly more than one half of the first derivative ESR spectrum of 5-t-butyl-2,3-diphenyltetrazolinyl (Id) in benzene solution.

The ESR hyperfine splitting constants of the tetrazolinyls (Ia–f) are summarized in Table 2. The assignment of the splittings was done by comparison with the ESR data of other tetrazolinyls.[6] Fig 2 gives as an example one half of the ESR spectrum of Id. The data of Table 2 show that the substituent R significantly affects only the splitting $a^{N2,3}$. The values of $a^{N2,3}$ vary from 8·3 gauss with R = OMe to 6·1 gauss

TABLE 2. ESR HYPERFINE SPLITTING CONSTANTS (GAUSS) OF THE TETRAZOLINYL RADICALS Ia–f IN BENZENE SOLUTION

	R	$a^{N_{1,4}}$	$a^{N_{2,3}}$	a^{H_o}	a^{H_m}
Ia	NO_2	5·6	6·1	1·0	0·5
Ib	CN	5·6	6·7	Not resolved	
Ic	$COOCH_3$	5·7	6·8	1·0	0·5
Id	H	5·7	7·5	0·95	0·5
Ie	CH_3	5·7	7·7	Not assigned	
If	OCH_3	5·7	8·3	Not assigned	

with R = NO_2. The spin densities at N-2 and N-3 correlate with the Hammett σ constant consistent with free radicals of type O.[12]

Phototetrazolinyl or 2,3-[*biphenylene*-(2,2)]*tetrazolinyl radicals* (II)

The reduction of the phototetrazolium salts (VIb–e) with sodium dithionite in a nitrogen atmosphere[8] gives the corresponding phototetrazolinyls. The radicals IIb and IIc were obtained as green-black needles of high purity, IId as blue needles[14] and IIe only in benzene solution. The stability of these phototetrazolinyls increases as the electron withdrawing power of the substituent R increases.

Phototetrazolinyls are known to be monomeric in some cases.[9, 18] Magnetic measurements of IIc yielded the following magnetic moments μ_{eff}/μ_B: 1·73 at 298°K, 1·73 at 195°K and 1·73 at 77°K corresponding to a free radical content of 100%. IIc does not dimerize, associate or disproportionate in the solid state or in solution (verified by low temperature UV spectra) at temperatures down to 77°K.

The UV absorption data of the phototetrazolinyls (IIb–e) are summarized in Table 3. The spectra show a remarkably large number of bands, especially in the UV region, due to the large tetracyclic conjugation system. The first absorption band of these radicals lies in the region of 600–700 mμ. Substitution of IId by the strong electron withdrawing substituent CN causes a bathochromic shift of the first band from 608 to 695 mμ. However, a bathochromic shift of smaller extent is also observed when the hydrogen is replaced by the weak electron donating substituent Me, a result not observed in radicals of type O.[12]

TABLE 3. UV ABSORPTION DATA OF THE PHOTOTETRAZOLINYLS (IIb–e) IN DIOXANE SOLUTION

	R	λ_{max} in mμ (log ε)							
IIb	CN	257 (4·56)	273 (4·49)	294 (4·20)	303 (4·19)	364 (4·32)	418s (3·92)	486 (3·75)	695 (3·52)
IIc	$COOCH_3$	257 (4·58)	272 (4·55)	287 (4·24)	297 (4·27)	368 (4·29)	415s (3·91)	498 (3·82)	697 (3·54)
IId	H		267 (4·49)	290 (4·27)	333 (4·08)	372 (3·75)	400 (3·72)		608 (3·3)
IIe	CH_3								625[a] (>3·0)

[a] in benzene

TABLE 4. ESR HYPERFINE SPLITTING CONSTANTS (GAUSS) OF THE PHOTOTETRAZOLINYLS (IIb-e) IN BENZENE SOLUTION

	R	$a^{N_{1,4}}$	$a^{N_{2,3}}$	a^{H}
IIb	CN	3·8	5·6	1·8 (2H)
IIc	$COOCH_3$	3·8	5·7	1·9 (2H)
IId	H	3·8	7·6	1·9 (4H)
IIe	CH_3	3·8	7·8	1·95 (8H)

The ESR hyperfine splitting constants of IIb–e are shown in Table 4. The assignments of the nitrogen splittings follow from data of ^{15}N labelled phototetrazolinyls.[11] The 1·8, 1·9 gauss splittings in IIb and IIc respectively are obviously connected with the hydrogens at the 3 and 3′ positions of the biphenylene part of the molecule. In the same way the observed hydrogen splittings of IId are assigned to the hydrogens at the 3,3′,5 and 5′ positions and the splittings of IIe to the hydrogens at the 3 and 3′ positions and to the Me groups in the 5 and 5′ positions. The resolution of the ESR spectra of IIb–e is not good enough to show clearly the splittings of the hydrogens in the 4,4′,6 and 6′ positions. As in the tetrazolinyl series the N-1 and N-4 nitrogen splittings of the phototetrazolinyls IIb–e are not effected by varying substitution in 5 and 5′ positions, while the N-2 and N-3 nitrogen splittings are changed in a Hammett relationship ($CH_3 > H > COOCH_3 > CN$).

CONCLUSION

The stability of tetrazolinyl and phototetrazolinyl radicals increases as the electron withdrawing power of the aryl groups at N-2 and N-3 increases. Electron accepting substituents lower the spin densities at these nitrogens. Radicals of high stability, e.g. Ia, IIb, are obtained when nearly equal spin densities at the nitrogen pairs N-1, N-4 and N-2, N-3 are observed. Therefore spin density delocalization governs the stability in these radical series.

Hammett's relationship evidently applies to tetrazolinyl and phototetrazolinyl ESR data, indicating that these radicals should be classified as O radicals. However, the inconsistent UV data of the phototetrazolinyls raise some doubt as to this assignment. One should consider the possibility that the UV absorption may not be a criterion for the classification of radicals in type O or type S.

EXPERIMENTAL

1,1-*Bis(4-nitrophenylazo)neopentane* (IIIa). The mixture of 4-nitraniline (3·5 g) in H_2O (10 ml) + conc HCl (10 ml) was cooled to 0° and kept at this temp while the soln of $NaNO_2$ (1·9 g) in H_2O (5 ml) was added dropwise under stirring. This diazonium salt soln was added in small portions to the stirred soln of pivaldehyde-4-nitrophenylhydrazone (5·5 g) in DMF* (40 ml) and pyridine (15 ml) kept at 0°. After 10 min the separated product (IIIa) was collected, washed with H_2O and MeOH and recrystallized from acetone–MeOH to yield yellow prisms (4·6 g), m.p. 121–122° (dec). (Found: C, 54·99; H, 4·75; N, 22·78. $C_{17}H_{18}N_6O_4$ requires: C, 55·13; H, 4·90; N, 22·69%).

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* Dimethylformamide.

1,1-*Bis(4-cyanophenylazo)neopentane* (IIIb). 4-Cyanoaniline (3·25 g) in H_2O (10 ml) + conc HCl (10 ml), $NaNO_2$ (1·9 g) in H_2O (5 ml) and pivaldehyde-4-cyanophenylhydrazone[*] (5·5 g) in DMF (40 ml) + pyridine (15 ml) were treated as above (IIIa). From acetone–MeOH yellow crystals (5·8 g) m.p. 134–135° (dec) were obtained. (Found: C, 69·33; H, 5·42; N, 25·37. $C_{19}H_{18}N_6$ requires: C, 69·07; H, 5·49; N, 25·44%).

1,1-*Bis(4-methoxycarbonylphenylazo)neopentane* (IIIc). The soln of 4-methoxycarbonylphenylhydrazine (5 g) and pivaldehyde (2·85 g) in EtOH (10 ml) was heated to the b.p., cooled (the pivaldehyde-4-methoxycarbonylphenylhydrazone[†] ppts), diluted with DMF (50 ml) and pyridine (25 ml), kept at 0° while 4-methoxycarbonylphenyldiazonium chloride (10 g) were added in small portions under stirring and worked up as above (IIIa). From acetone–MeOH yellow crystals (7 g) m.p. 118–120° (dec) were obtained. (Found: C, 63·72; H, 6·11; N, 13·88. $C_{21}H_{24}N_4O_4$ requires: C, 63·62; H, 6·10; N, 14·13%).

1,1-*Di*-p-*tolylazo-neopentane* (IIIe). *p*-Toluidine (5·35 g) in H_2O (7·5 ml) + conc HCl (12·5 ml), $NaNO_2$ (3·45 g) in H_2O (10 ml); *p*-tolylhydrazine (6·6 g) + pivaldehyde (4·1 g) in EtOH (15 ml) heated to the b.p., cooled and diluted with DMF (50 ml) and pyridine (25 ml were treated as above (IIIa, IIIc). The product separated upon addition of H_2O to the mixture. From acetone–MeOH yellow crystals (14 g) m.p. 62–63 (dec) were obtained. (Found: C, 73·79; H, 7·60; N, 18·20. $C_{19}H_{24}N_4$ requires: C, 73·99; H, 7·84; N, 18·17%).

1,1-*Bis(4-methoxyphenylazo)neopentane* (IIIf). *p*-Anisidine (11·9 g) in H_2O (15 ml) + conc HCl (25 ml), $NaNO_2$ (7·5 g) in H_2O (20 ml); 4-methoxyphenylhydrazine (13·8 g) + pivaldehyde (8·6 g) in EtOH (25 ml), DMF (100 ml) + pyridine (50 ml) were treated as above (IIIc). From acetone–MeOH yellow plates (17·3 g), m.p. 90–91° (dec) were obtained. (Found: C, 66·91; H, 7·08; N, 16·51. $C_{19}H_{24}N_4O_2$ requires: C, 67·03; H, 7·11; N, 16·46%).

3-*t-Butyl*-1,5-*bis(4-nitrophenyl)formazan* (IVa). The soln of crude IIIa (4 g) in pyridine (40 ml) was left at room temp for 10 hr. The separated material yielded from DMF–MeOH dark violet prisms (2·6 g), m.p. 212–213° (dec). (Found: C, 55·42; H, 5·08; N, 22·64. $C_{17}H_{18}N_6O_4$ requires: C, 55·13; H, 4·90; N, 22·69%); λ_{max}^{dioxan} 490 mμ (log ε 4·43), 340 (4·09), 312 (4·11), 226 (4·14).

3-*t-Butyl*-1,5-*bis(4-cyanophenyl)formazan* (IVb). Crude IIIb (5·7 g) in pyridine (25 ml) were treated as above (IVa). From acetone dark red crystals (4·4 g), m.p. 204–205° (dec) were obtained. (Found: C, 68·81; H, 5·77; N, 25·47. $C_{19}H_{18}N_6$ requires: C, 69·07; H, 5·49; N, 25·44%).

3-*t-Butyl*-1,5-*bis(4-methoxycarbonylphenyl)formazan* (IVc). Crude IIIc (4·5 g) in DMF (150 ml) + KOMe (0·75 g) were vigorously stirred for 15 min under N_2, 2N HCl (10 ml) and H_2O were added and the separated product was collected. From DMF–MeOH dark red crystals (4·2 g), m.p. 165–166° (dec) were collected. (Found: C, 63·46; H, 5·85; N, 14·13. $C_{21}H_{24}N_4O_4$ requires: C, 63·62; H, 6·10; N, 14·13%).

3-*t-Butyl*-1,5-*di*-p-*tolylformazan* (IVe). Crude IIIe (4·5 g) in DMF (150 ml) + KOMe (1 g) were treated as above (IVc). From EtOH dark red crystals (3·9 g), m.p. 99–100° (dec) were obtained. (Found: C, 73·73; H, 8·04; N, 18·28. $C_{19}H_{24}N_4$ requires: C, 73·99; H, 7·84; N, 18·17%).

3-*t-Butyl*-1,5-*bis(4-methoxyphenyl)formazan* (IVf). Crude IIIf (3 g) in DMF (100 ml) + KOMe (0·5 g) were treated as above (IVc). From MeOH dark red crystals (2·6 g), m.p. 93–94°) (dec) were obtained. (Found: C, 66·92; H, 7·11; N, 16·32. $C_{19}H_{24}N_4O_2$ requires: C, 67·03; H, 7·11; N, 16·46%).

5-*t-Butyl*-2,3-*bis(4-nitrophenyl)tetrazolium bromide* (Va). The soln of N-bromosuccinimide (1·45 g) in EtOAc (100 ml) was added to IVa (3 g) in EtOAc (200 ml), and the mixture was stirred for 12 hr, colourless crystals (3·4 g) separated, m.p. 260–261° (dec). (Found: C, 45·59; H, 3·69; N, 18·65. $C_{17}H_{17}BrN_6O_4$ requires: C, 45·45; H, 3·81; N, 18·71%); λ_{max}^{EtOH} 285 mμ (log ε 4·11), 247 (4·33).

5-*t-Butyl*-2,3-*bis(4-nitrophenyl)tetrazolium nitrate*. $AgNO_3$ (1·13 g) dissolved in DMF (20 ml) were added to the soln of Va (3 g) in DMF (25 ml). The separated AgBr was collected and ether was added to the filtrate. The product yielded from MeOH–ether colourless prisms (2·4 g) m.p. 232° (dec). (Found: C, 47·04; H, 4·01; N, 22·58. $C_{17}H_{17}N_7O_7$ requires: C, 47·33; H, 3·97; N, 22·43%).

5-*t-Butyl*-2,3-*bis(4-cyanophenyl)tetrazolium bromide* (Vb). N-bromosuccinimide (1·45 g) in EtOAc (100 ml) + IVb (2·5 g) in EtOAc (100 ml), were treated as above (Va) for 1 hr and yielded colourless prisms (2·9 g), m.p. 276–277° (dec). Found: C, 55·45; H, 4·42; N, 20·24. $C_{19}H_{17}BrN_6$ requires: C, 55·75; H, 4·19; N, 20·53%).

5-*t-Butyl*-2,3-*bis(4-methoxycarbonylphenyl)tetrazolium bromide* (Vc). N-bromosuccinimide (1·85 g) in EtOAc (150 ml) + IVc (4 g) in EtOAc (200 ml), were treated as above (Va) for 3 hr and yielded colourless

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[*] M.p. 152–153° (dec). (Found: C, 75·95; H, 5·12; N, 19·27. $C_{14}H_{11}N_3$ requires: C, 75·99; H, 5·01; N, 18·99%).

[†] M.p. 123–125° (dec). (Found: C, 66·81; H, 7·93; N, 11·75. $C_{13}H_{18}N_2O_2$ requires: C, 66·64; H, 7·74; N, 11·96%).

prisms (4·4 g), m.p. 248–249° (dec). (Found: C, 53·04; H, 4·80; N, 11·78. $C_{21}H_{23}BrN_4O_4$ requires: C, 53·06; H, 4·88; N, 11·79%).

5-t-Butyl-2,3-di-p-tolyltetrazolium chloride (Ve). Dry HCl gas was bubbled into the stirred mixture of IVe (3·08 g) and i-amyl nitrite (1·5 g) in $CHCl_3$ (20 ml) until the formazan colour disappeared. The salt was separated by addition of ether. From MeOH–EtOAc–ether colourless prisms (2·1 g), m.p. >300° were obtained. (Found: C, 66·69; H, 6·84; N, 16·50. $C_{19}H_{23}ClN_4$ requires: C, 66·56; H, 6·76; N, 16·34%).

5-t-Butyl-2,3-bis(4-methoxyphenyl)tetrazolium bromide (Vf). N-bromosuccinimide (1·78 g) in EtOAc (100 ml) + IVf (3·4 g) in EtOAc (50 ml), were treated as above (Va) for 24 hr yielding colourless crystals (4 g), m.p. 234–235° (dec). (Found: C, 54·55; H, 5·60; N, 13·26. $C_{19}H_{23}BrN_4O_2$ requires: C, 54·42; H, 5·53; N, 13·36%).

5-t-Butyl-2,3[5,5′-dicyanobiphenylene(2,2′)]tetrazolium nitrate (VIb) *and 2,9-dicyanobenzo[c]cinnoline.* The soln of Vb (2·04 g) in EtOH (300 ml) + H_2O (700 ml) + 2N HNO_3 (40 ml) in a quartz vessel was irradiated with 2537 Å lamps in the Rayonet Reactor RPR 208 for 1 day while N_2 was bubbled through the soln. The reaction mixture was concentrated to 200 ml by evaporation in vacuum (bath temp <35°). The separated product was collected and yielded from DMF 2,9-dicyanobenzo[*c*]cinnoline (0·4 g), m.p. >360°. (Found: C, 73·31; H, 2·92; N, 24·52. $C_{14}H_6N_4$ requires: C, 73·03; H, 2·63; N, 24·34%). The filtrate was further concentrated to 20 ml by evaporation in vacuum (bath temp <35°) and the separated product recrystallized from DMF–MeOH: yielding VIb (0·55 g), m.p. >360°. (Found: C, 58·88; H, 3·93; N, 25·11. $C_{19}H_{15}N_7O_3$ requires: C, 58·60; H, 3·88; N, 25·18%).

5-t-Butyl-2,3[5,5′-dimethoxycarbonylbiphenylene(2,2′)]tetrazolium nitrate (VIc) *and 2,9-dimethoxycarbonylbenzo*[c]*cinnoline.* Compound Vc (4 g) in EtOH (120 ml) + H_2O (320 ml) + 2N HNO_3 (20 ml) were treated as above (VIb). The first separated product recrystallized from DMF–MeOH gave 2,9-dimethoxycarbonylbenzo[*c*]cinnoline (0·32 g), m.p. 220–222°. (Found: C, 65·09; H, 4·09; N, 9·15. $C_{16}H_{12}N_2O_2$ requires: C, 64·86; H, 4·08; N, 9·46%). The second separated product recrystallized from MeOH–EtOAc yielded VIc (1·6 g), m.p. >300°. (Found: C, 55·18; H, 4·74; N, 15·17. $C_{21}H_{21}N_5O_7$ requires: C, 55·38; H, 4·65; N, 15·38%).

5-t-Butyl-2,3[5,5′-dimethylbiphenylene(2,2′)]tetrazolium nitrate (VIe). Compound Ve (1 g) in EtOH (500 ml) + H_2O (500 ml) + 2N HNO_3 (20 ml) were treated as above (VIb) for 2 days. The mixture was concentrated to 50 ml by evaporation in vacuum (bath temp <30°). The separated product yielded from EtOH–EtOAc colourless crystals (0·3 g) of VIe, m.p. >300°. (Found: C, 61·99; H, 5·88; N, 19·07. $C_{19}H_{21}N_5O_3$ requires: C, 62·11; H, 5·76; N, 19·06%).

5-t-Butyl-2,3-bis(4-nitrophenyl)tetrazolinyl (Ia). The soln of IVa (1 g) and tetra-*p*-tolylhydrazine (1 g) was left at 30° for 1 day. Then tetra-*p*-tolylhydrazine (1 g) was added and the soln warmed to 45° for 30 min. The mixture was evaporated in vacuum (bath temp <30°) and the crystallized residue treated with ligroin. The remaining green crystals (0·95 g) of Ia melted at 125–126° (dec). Recrystallization from cold benzene–ligroin gave green-black needles, m.p. 126–127° (dec). Found: C, 55·06; H, 4·68; N, 22·95. $C_{17}H_{17}N_6O_4$ requires: C, 55·28; H, 4·64; N, 22·75%); λ_{max}^{dioxan} 590 mμ (log ε 3·59), 432 (4·05), 385 (4·01), 276 (4·18).

Tetrazolinyls (Ib–f). These tetrazolinyl radicals were generated by reaction of formazan IV (0·01 mol) in benzene (2 ml) with tetra-*p*-tolylhydrazine (0·05 mol) in benzene (2 ml). The mixture was heated to 60° for 10 sec. The red-brown colour of the soln changed to greenish brown after completion of the reaction.

Decomposition of Ia *in* MeOH. A suspension of Ia (100 mg) in MeOH (50 ml) was stirred for 30 min, evaporated in vacuum and the residue chromatographed on Al_2O_3 (Brockmann) to give upon elution with benzene formazan IVa (52 mg, 54%) from DMF–MeOH, m.p. 206–208° (dec), and a colourless compound, 5-t-butyl-2(4-nitrophenyl)tetrazole (VIIa; 18 mg, 27%), from MeOH m.p. 154–156° (dec). (Found: mol. weight 241; C, 53·03; H, 5·06; N, 28·20. $C_{11}H_{13}N_5O_2$ (247·3) requires: C, 53·43; H, 5·30; N, 28·33%); NMR: 9 t-butyl protons 1·6 ppm (singlet), 4 aromatic protons 8·4 ppm (multiplet).

3-t-Butyl-6-nitro-1,2,4-benzotriazine. The mixture of IVa (1 g) in glacial AcOH (10 ml) + conc H_2SO_4 (10 ml) was stirred for 5 min, poured into water and extracted with ether. The ether layer was washed with H_2O, evaporated in vacuum and the residue was chromatographed on Al_2O_3 (Brockmann) to give upon elution with benzene *p*-nitraniline (180 mg, 40%); from benzene–ligroin yellow crystals, m.p. 145–146°, and 3-t-butyl-6-nitro-1,2,4-benzotriazine (140 mg, 22%) as orange needles from MeOH m.p. 91–92°. (Found: C, 57·48; H, 5·25; N, 24·28. $C_{11}H_{12}N_4O_2$ requires: C, 56·89; H, 5·21; N, 24·13%); NMR: 9-t-butyl protons 1·7 ppm (singlet), 3 aromatic protons 8–9 ppm (multiplet).

5-t-Butyl-2,3[5,5′-dicyanobiphenylene(2,2′)]tetrazolinyl (IIb). A soln of sodium dithionite (1 g) in aqueous 1N Na_2CO_3 (40 ml), was added to a suspension of VIb (200 mg) in H_2O (100 ml) + benzene (100 ml) in a separatory funnel while N_2 was bubbled through the mixture. After shaking for 5 min the aqueous layer was separated, the benzene layer was washed with H_2O and evaporated in vacuum (bath temp <30°). The residue yielded from benzene–ligroin green–black needles (80 mg), m.p. 289–292° (dec). (Found: C, 69·44; H, 4·33; N, 25·12. $C_{19}H_{15}N_6$ requires: C, 69·71; H, 4·62; N, 25·67%).

5-t-Butyl-2,3[5,5'-dimethoxycarbonylbiphenylene(2,2')] tetrazolinyl (IIc). Compound VIc (300 mg) in H_2O (100 ml) + benzene (100 ml), sodium dithionite (1 g) in aqueous 1N Na_2CO_3 (40 ml) were treated as in the preparation of IIb. From benzene–ligroin green–black needles (190 mg), m.p. 254–255° (dec) were obtained. (Found: C, 64·02; H, 5·23; N, 14·34. $C_{21}H_{21}N_4O_4$ requires: C, 64·11; H, 5·38; N, 14·24%).

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