Structure of the Reaction Products from Dehydroascorbic Acid Analogues, *o*-Phenylenediamine, and Arylhydrazines. X-Ray Molecular Structure of 3-[L-*threo*-2,3,4-Triacetoxy-1-(phenylhydrazono)butyl]quinoxalin-2(1*H*)-one Hemihydrate[1,2]

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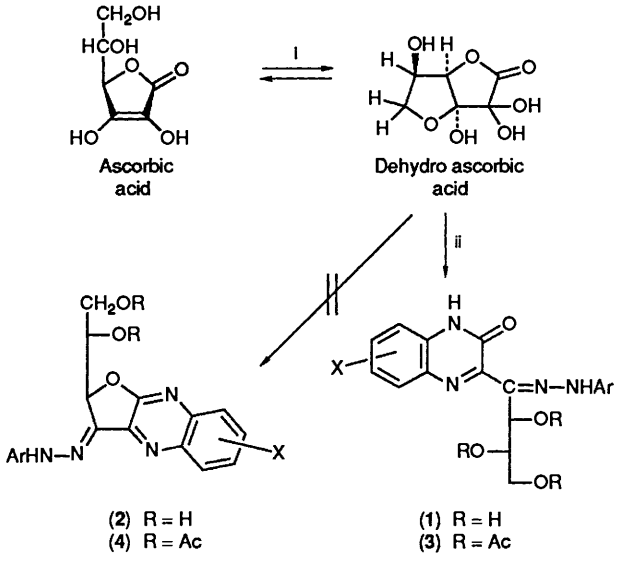
Acetylation of the product obtained from successive reaction of dehydro-L-ascorbic acid with *o*-phenylenediamine and phenylhydrazine gave 3-[L-*threo*-2,3,4-triacetoxy-1-(phenylhydrazono)butyl]-quinoxalin-2(1*H*)-one (**3**) rather than the cyclic structure (**4**) previously assigned for the reaction product. The structure of compound (**3**) was confirmed based on ^{1}H NMR, ^{13}C NMR, and X-ray analysis. Reinvestigation of the reaction of 5-phenylfuran-2,3,4(5*H*)-trione (**6**) with *o*-phenylenediamine and an arylhydrazine led to the isolation of two components (**7**) and (**10**). The former was found to exist in dimethyl sulphoxide solution as a tautomeric mixture of hydrazone imine and diazenyl enamine. Attempted acetylation of compound (**7**) afforded the furo[2,3-*b*]quinoxaline ring system (**8**).

The structure of the product from the successive reaction of dehydro-L-ascorbic acid with *o*-phenylenediamine and phenylhydrazine has been established as 3-[L-*threo*-2,3,4-trihydroxy-1-(phenylhydrazono)butyl]quinoxalin-2(1*H*)-one[3] (**1**) and not the corresponding anhydro structure (Scheme 1) which in 1959 had been assigned[4] to the product based on its conversion into a diacetate (**4**) on the basis of its elemental analysis.

Although we had provided definitive proof of structure (**1**) we decided to re-examine the acetylation of compound (**1**) under the conditions reported by the earlier investigators[4] in order to gain a better understanding of the reactivity of this particular molecule which has been used as precursor for pyrazole, flavazole, and pyridazinone heterocycles.[3,5,6] Thus, treatment of compound (**1**) with acetic anhydride–pyridine mixture afforded, in our hands, a red compound of m.p. 136–138 °C whose elemental analysis and ^{1}H and ^{13}C NMR spectra confirmed its structure as the hemihydrate of the triacetate (**3**). The principal argument is based on the presence of three different acetyl groups, responsible for signals at δ 2.05, 2.06, and 2.15 (300 MHz; $CDCl_3$) and for the resonances found at δ 4.55 (2 H), 6.05 (1 H), and 7.03 (1 H). Two signals exchangeable with D_2O at δ 12.31 and 14.42 ruled out *N*-acetylation. The hemihydrated molecule of water caused a broad signal of one-proton intensity and its chemical shift was found to be concentration dependent. The ^{13}C NMR spectrum (100.6 MHz) showed signals at δ 20.85, 21.04 21.18, 63.41, 71.92 and 71.94 easily assigned to the three acetate methyls, the CH_2O, and the two CHO groups.† An X-ray diffraction study of compound (**3**) furnished a final unambiguous proof for its structure and hence that of its precursor (**1**). A perspective view of the two molecules A and B in the unit cell of compound (**3**) is presented in Figures 1 and 2, while the co-crystallized water molecule was found to form a weak hydrogen bond (Figure 3). Final atomic co-ordinates are given in Tables 1 and 2 and bond distances and bond angles in Tables 3 and 4. Isotropic thermal parameters and hydrogen atom co-ordinates are available on request from the Cambridge Crystallographic Data Centre.‡ The triacetate (**3**) exists in the hydrazone imine tautomeric form in the solid state (see below).

Compound (**3**) was heat sensitive and underwent dehydroacetylative cyclization to 3-[5-(acetoxymethyl)-1-phenylpyrazol-3-yl]quinoxalin-2(1*H*)-one (**5**) upon pyrolysis either neat or in boiling methanol. Earlier investigators reported a compound with m.p. 182 °C and assigned it structure (**4**).[4] Its composition and the way it was prepared suggest that it may have been an intermediate in the conversion of (**3**) into (**5**).



Scheme 1. *Reagents:* i, *p*-benzoquinone; ii, 1,2-$(NH_2)_2C_6H_3X$.

Attention was then turned to other dehydroascorbic analogues, such as the trione (**6**) (5-phenylfuran-2,3,4(5*H*)-trione), which had provided 3-[2-hydroxy-2-phenyl-1-(phenylhydrazono)ethyl]quinoxalin-2(1*H*)-one (**7a**).[7] The ^{1}H NMR spectrum of compound (**7a**) revealed that in $(CD_3)_2SO$ solution it exists

† Copies of the spectra are available as a supplementary publication [SUP No. 56786 (5 pp.)].†

‡ See 'Instructions for Authors (1990),' *J. Chem. Soc., Perkin Trans. 1*, 1990, Issue 1.

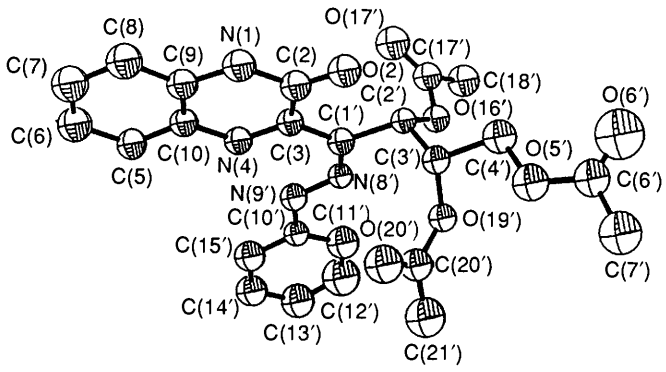


Figure 1. Perspective drawing of compound (**3**) (molecule A) with atom-labelling scheme.

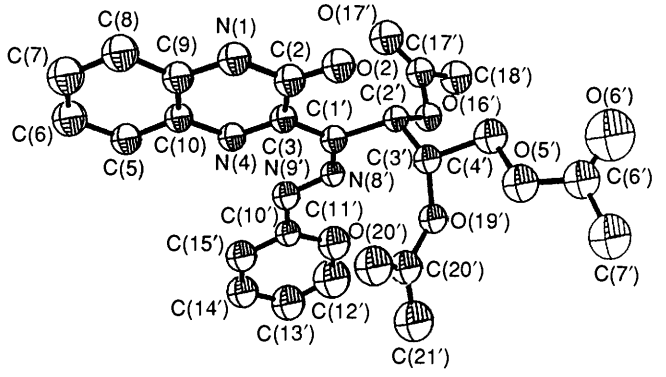


Figure 2. Perspective drawing of compound (**3**) (molecule B) with atom-labelling scheme.

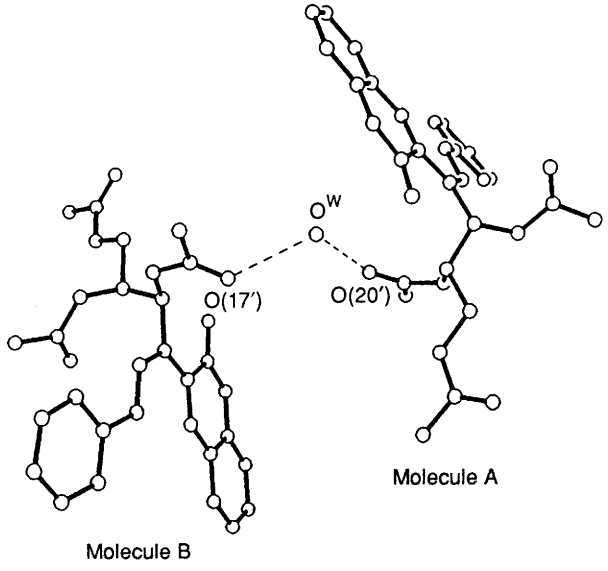
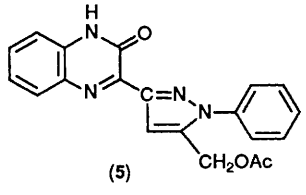
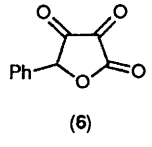


Figure 3. Projection of the molecular structure showing the intermolecular hydrogen bonding [distances and angle for $O(20'_A)$–O–$O(17'_B)$ are 2.75(2) and 2.81(2) Å and 110.7(5)°].



(5)

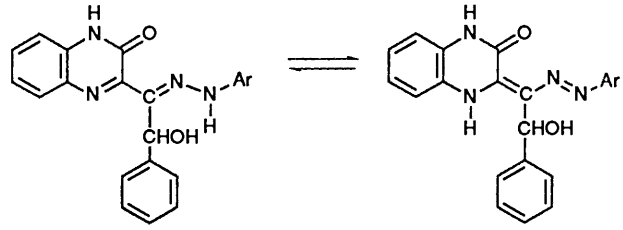


(6)

Table 1. Fractional atomic co-ordinates ($\times 10^4$) for compound (**3**) (molecule A).

Atom	*x*	*y*	*z*
N(1)	215(7)	3 402(*)	5 825(13)
C(2)	801(9)	3 844(11)	6 658(16)
O(2)	792(6)	4 554(9)	6 543(10)
C(3)	1 436(8)	3 381(11)	7 636(14)
N(4)	1 358(7)	2 618(9)	7 835(11)
C(5)	623(9)	1 418(11)	7 249(16)
C(6)	−3(10)	1 000(12)	6 385(17)
C(7)	−530(10)	1 383(12)	5 324(18)
C(8)	−494(10)	2 196(12)	5 070(18)
C(9)	142(9)	2 605(10)	5 974(16)
C(10)	697(8)	2 223(10)	6 996(15)
C(1')	2 140(9)	3 765(10)	8 525(15)
C(2')	2 333(8)	4 635(10)	8 337(15)
C(3')	1 911(9)	5 142(10)	9 355(14)
C(4')	2 066(10)	6 002(11)	9 110(17)
O(5')	1 646(7)	6 420(9)	10 203(11)
C(6')	1 770(11)	7 176(12)	10 382(19)
O(6')	2 190(10)	7 523(12)	9 600(18)
C(7')	1 369(11)	7 512(13)	11 601(19)
N(8')	2 705(7)	3 424(9)	9 534(11)
N(9')	2 641(7)	2 672(9)	9 866(12)
C(10')	3 187(9)	2 352(10)	11 047(15)
C(11')	3 845(10)	2 780(12)	11 748(18)
C(12')	4 379(13)	2 417(14)	12 940(22)
C(13')	4 227(11)	1 675(13)	13 391(20)
C(14')	3 583(10)	1 252(12)	12 630(18)
C(15')	3 059(10)	1 597(11)	11 435(17)
O(16')	3 196(5)	4 797(9)	8 638(10)
C(17')	3 652(9)	4 617(11)	7 541(17)
O(17')	3 400(7)	4 283(9)	6 411(12)
C(18')	4 521(9)	4 860(12)	8 008(18)
O(19')	2 254(5)	4 971(8)	10 922(10)
C(20')	1 762(10)	4 666(11)	11 819(17)
O(20')	1 033(7)	4 515(9)	11 382(12)
C(21')	2 165(11)	4 510(13)	13 351(18)

* Parameter constrained to define the origin in the monoclinic space group $P2_1$ (No. 4).



hydrazone imine form
A

diazenyl enamine form
B

as a tautomeric mixture of the hydrazone imine form A and the diazenyl enamine form B in the ratio 3:2. Form A of (**7a**) was responsible for two doublets at δ 5.73 and 5.90 ($J \sim 7$ Hz) for the CHOH protons, which collapsed to a singlet upon addition of D_2O, but which did not integrate for one proton. The same system of B form was hidden under the protons of the aromatic region. That three different NH protons were present was shown by downfield signals at δ 10.47 (N–NH), 10.63 [N(4)–H], and 11.47 [N(1)–H]. The ^1H NMR spectra of compounds (**7b–c**) behaved similarly (see Experimental section). The assignment of the two forms as hydrazone ⇄ azo was preferred as given for similar compounds[8] over the *syn* and *anti* isomers as given for the corresponding methyl analogues.[9]

Attempted acetylation of compound (**7a**) with acetic anhydride in pyridine at room temperature or with refluxing acetic

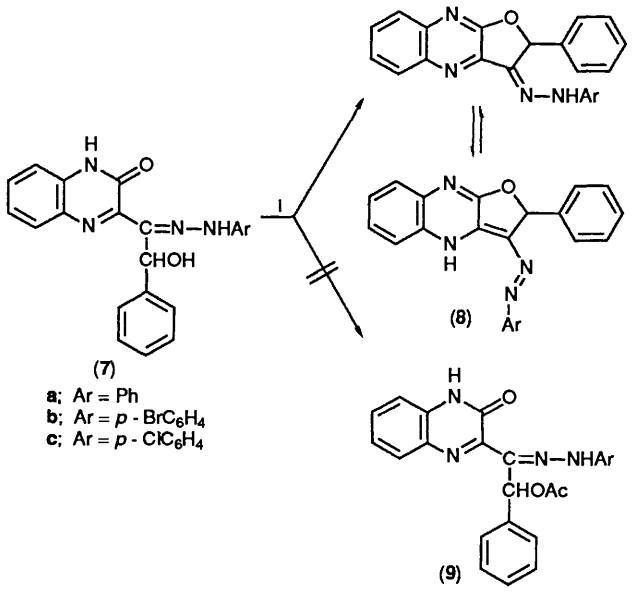
Table 2. Fractional atomic co-ordinates ($\times 10^4$) for compound (3) (molecule B).

Atom	*x*	*y*	*z*
N(1)	−987(8)	5 212(10)	6 592(13)
C(2)	−1 467(9)	4 889(11)	5 388(16)
O(2)	−1 371(7)	4 181(9)	5 082(12)
C(3)	−2 071(8)	5 393(10)	4 520(14)
N(4)	−2 097(7)	6 149(10)	4 832(12)
C(5)	−1 623(10)	7 255(11)	6 384(18)
C(6)	−1 122(10)	7 538(13)	7 611(19)
C(7)	−585(11)	7 081(13)	8 513(21)
C(8)	−534(11)	6 293(12)	8 234(19)
C(9)	−1 028(10)	5 982(11)	6 965(18)
C(10)	−1 588(10)	6 459(11)	6 063(17)
C(1′)	−2 639(9)	5 118(11)	3 250(15)
C(2′)	−2 620(9)	4 282(11)	2 706(14)
C(3′)	−3 148(9)	3 769(10)	3 623(16)
C(4′)	−3 043(10)	2 907(11)	3 313(17)
O(5′)	−3 356(6)	2 523(10)	4 554(12)
C(6′)	−3 212(12)	1 764(14)	4 798(22)
O(6′)	−2 901(11)	1 406(13)	3 899(19)
C(7′)	−3 533(11)	1 425(13)	6 100(20)
N(8′)	−3 256(7)	5 522(9)	2 475(12)
N(9′)	−3 381(7)	6 265(10)	2 834(12)
C(10′)	−4 109(9)	6 655(11)	2 142(16)
C(11′)	−4 647(10)	6 299(11)	1 007(16)
C(12′)	−5 334(11)	6 733(12)	368(20)
C(13′)	−5 500(12)	7 457(13)	899(19)
C(14′)	−4 972(12)	7 772(14)	2 052(22)
C(15′)	−4 238(11)	7 396(12)	2 707(19)
O(16′)	−2 986(5)	4 199(9)	1 143(9)
C(17′)	−2 490(10)	4 362(11)	144(17)
O(17′)	−1 791(8)	4 617(10)	516(13)
C(18′)	−2 881(11)	4 212(13)	−1 402(18)
O(19′)	−3 997(6)	3 963(8)	3 232(10)
C(20′)	−4 362(9)	4 405(11)	4 222(17)
O(20′)	−4 012(7)	4 586(10)	5 422(13)
C(21′)	−5 218(10)	4 614(13)	3 552(20)
O(w)	−339(8)	4 305(10)	9 258(13)

* Parameter constrained to define the origin in the monoclinic space group $P2_1$ (No. 4).

Table 3. Bond distances (Å) for compound (3)·0.5H_2O.

Molecule A		Molecule B	
N(1)–C(2)	1.357(18)	N(1)–C(2)	1.354(19)
N(1)–C(9)	1.375(17)	N(1)–C(9)	1.363(26)
C(2)–O(2)	1.219(24)	C(2)–O(2)	1.255(24)
C(2)–C(3)	1.485(21)	C(2)–C(3)	1.450(21)
C(3)–N(4)	1.325(24)	C(3)–N(4)	1.323(24)
C(3)–C(1′)	1.457(20)	C(3)–C(1′)	1.438(19)
N(4)–C(10)	1.398(18)	N(4)–C(10)	1.386(19)
C(5)–C(6)	1.388(22)	C(5)–C(6)	1.359(23)
C(5)–C(10)	1.402(25)	C(5)–C(10)	1.394(27)
C(6)–C(7)	1.355(23)	C(6)–C(7)	1.352(26)
C(7)–C(8)	1.410(28)	C(7)–C(8)	1.375(29)
C(8)–C(9)	1.407(22)	C(8)–C(9)	1.399(23)
C(9)–C(10)	1.359(20)	C(9)–C(10)	1.393(23)
C(1′)–C(2′)	1.535(24)	C(1′)–C(2′)	1.510(25)
C(1′)–N(8′)	1.330(18)	C(1′)–N(8′)	1.331(19)
C(2′)–C(3′)	1.490(21)	C(2′)–C(3′)	1.541(22)
C(2′)–O(16′)	1.423(15)	C(2′)–O(16′)	1.442(15)
C(3′)–C(4′)	1.512(25)	C(3′)–C(4′)	1.513(25)
C(3′)–O(19′)	1.458(15)	C(3′)–O(19′)	1.420(17)
C(4′)–O(5′)	1.453(21)	C(4′)–O(5′)	1.438(21)
O(5′)–C(6′)	1.315(26)	O(5′)–C(6′)	1.332(29)
C(6′)–O(6′)	1.199(26)	C(6′)–O(6′)	1.176(29)
C(6′)–C(7′)	1.462(26)	C(6′)–C(7′)	1.458(29)
N(8′)–N(9′)	1.326(21)	N(8′)–N(9′)	1.332(22)
N(9′)–C(10′)	1.393(18)	N(9′)–C(10′)	1.425(20)
C(10′)–C(11′)	1.375(22)	C(10′)–C(11′)	1.384(21)
C(10′)–C(15′)	1.359(26)	C(10′)–C(15′)	1.390(27)
C(11′)–C(12′)	1.420(26)	C(11′)–C(12′)	1.398(24)
C(12′)–C(13′)	1.362(32)	C(12′)–C(13′)	1.366(30)
C(13′)–C(14′)	1.374(25)	C(13′)–C(14′)	1.356(26)
C(14′)–C(15′)	1.398(22)	C(14′)–C(15′)	1.412(26)
O(16′)–C(17′)	1.344(18)	O(16′)–C(17′)	1.313(19)
C(17′)–O(17′)	1.179(19)	C(17′)–O(17′)	1.223(21)
C(17′)–C(18′)	1.481(21)	C(17′)–C(18′)	1.457(21)
O(19′)–C(20′)	1.316(20)	O(19′)–C(20′)	1.360(20)
C(20′)–O(20′)	1.227(19)	C(20′)–O(20′)	1.181(19)
C(20′)–C(21′)	1.454(21)	C(20′)–C(21′)	1.484(22)



Scheme 2. *Reagents and conditions:* i, Ac_2O, heat.

anhydride did not afford the monoacetyl derivative but a product which has been assigned structure (**8a**) (Scheme 2). Structural proof of the fused system (**8**) rests on spectroscopic data as well as on elemental analysis. The IR spectrum showed the absence of the carbonyl amide and acetyl groups. In the ^1H NMR spectrum [$(CD_3)_2SO$] for (**8a**), two diagnostic singlets were observed for the C-2 methine proton at δ 6.70 and 6.90 (*ca.* 2:1) and two exchangeable singlets for the NH proton at δ 10.12 and 11.50 (*ca.* 1:2), confirming its existence in two different tautomeric states (*viz.* hydrazo ⇄ azo tautomers). The mass spectral (EI) abundance data for compound (**8a**) showed an intense peak at *m/z* 352 ($M^{\cdot+}$ $[C_{22}H_{16}N_4O]^+$, RI 41%), 261 ($M^+ - C_6H_5N^{\cdot}$, 11), 247 ($M^{\cdot+} - C_6H_5CO^{\cdot}$, 21), 245 ($M^+ - C_6H_5CHOH$, 12), and a base peak at *m/z* 77 ($C_6H_5^+$). The above data indicated that the loss of one molecule of water from compound (**7a**) occurred between the hydroxy group and the enolized amide group to afford the final product (**8a**). Reaction of compound (**8a**) with sodium hydroxide followed by acidification with acetic acid caused ring opening to give its precursor (**7a**).

Acetylation of compounds (**7b** and **c**) under the same conditions gave the corresponding furoquinoxalines (**8b** and **c**), whose treatment with alkali regenerated their precursors (**7b** and **c**).

The synthesis of compounds of type (**7**) was accompanied by a competing reaction yielding compounds of type (**10**) whose yields depended on the duration of the addition of arylhydrazine to the reaction mixture of (**6**) and the diamine. The observation of this side-reaction to give compound (**10**) is not

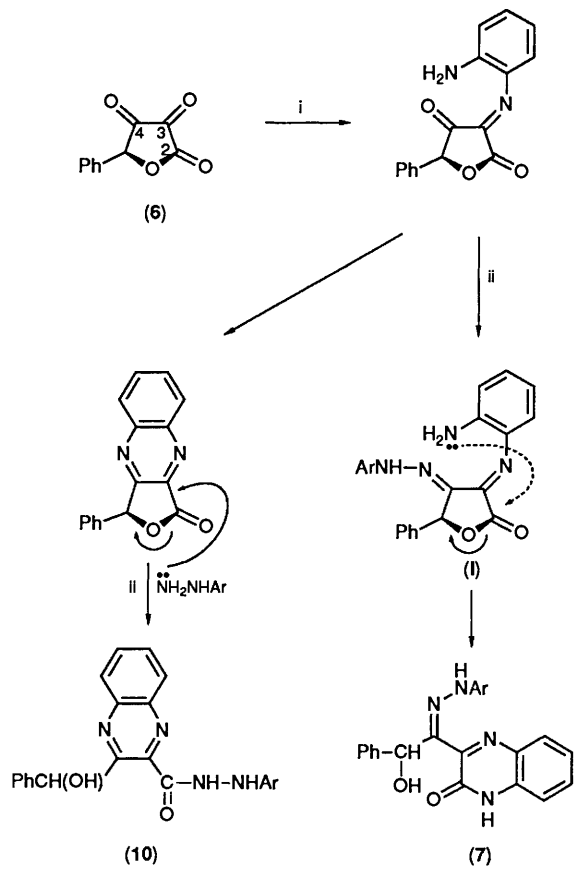
Table 4. Bond angles (°) for compound (3)·0.5H_2O.

Molecule A		Molecule B	
C(2)–N(1)–C(9)	124.2(12)	C(2)–N(1)–C(9)	123.0(14)
N(1)–C(2)–O(2)	120.6(12)	N(1)–C(2)–O(2)	119.3(14)
N(1)–C(2)–C(3)	113.9(15)	N(1)–C(2)–C(3)	117.1(16)
O(2)–C(2)–C(3)	125.4(14)	O(2)–C(2)–C(3)	123.7(13)
C(2)–C(3)–N(4)	122.1(13)	C(2)–C(3)–N(4)	120.6(12)
C(2)–C(3)–C(1′)	120.7(15)	C(2)–C(3)–C(1′)	122.7(16)
N(4)–C(3)–C(1′)	117.0(12)	N(4)–C(3)–C(1′)	116.6(13)
C(3)–N(4)–C(10)	119.0(12)	C(3)–N(4)–C(10)	120.4(13)
C(6)–C(5)–C(10)	119.3(14)	C(6)–C(5)–C(10)	118.3(16)
C(5)–C(6)–C(7)	119.0(18)	C(5)–C(6)–C(7)	122.7(20)
C(6)–C(7)–C(8)	123.5(16)	C(6)–C(7)–C(8)	120.6(17)
C(7)–C(8)–C(9)	116.2(14)	C(7)–C(8)–C(9)	118.4(16)
N(1)–C(9)–C(8)	120.2(13)	N(1)–C(9)–C(8)	121.4(15)
N(1)–C(9)–C(10)	118.8(13)	N(1)–C(9)–C(10)	118.4(14)
C(8)–C(9)–C(10)	120.9(16)	C(8)–C(9)–C(10)	120.1(17)
N(4)–C(10)–C(5)	117.7(13)	N(4)–C(10)–C(5)	119.9(15)
N(4)–C(10)–C(9)	121.3(15)	N(4)–C(10)–C(9)	120.4(17)
C(5)–C(10)–C(9)	121.0(13)	C(5)–C(10)–C(9)	119.7(14)
C(3)–C(1′)–C(2′)	122.4(12)	C(3)–C(1′)–C(2′)	121.5(13)
C(3)–C(1′)–N(8′)	126.1(16)	C(3)–C(1′)–N(8′)	126.6(16)
C(2′)–C(1′)–N(8′)	111.4(12)	C(2′)–C(1′)–N(8′)	111.8(12)
C(1′)–C(2′)–C(3′)	112.2(12)	C(1′)–C(2′)–C(3′)	109.3(12)
C(1′)–C(2′)–O(16′)	112.3(12)	C(1′)–C(2′)–O(16′)	112.2(13)
C(3′)–C(2′)–O(16′)	107.6(12)	C(3′)–C(2′)–O(16′)	105.6(11)
C(2′)–C(3′)–C(4′)	112.1(13)	C(2′)–C(3′)–C(4′)	111.9(13)
C(2′)–C(3′)–O(19′)	108.5(12)	C(2′)–C(3′)–O(19′)	109.5(12)
C(4′)–C(3′)–O(19′)	106.5(12)	C(4′)–C(3′)–O(19′)	108.3(13)
C(3′)–C(4′)–O(5′)	106.1(13)	C(3′)–C(4′)–O(5′)	104.1(13)
C(4′)–O(5′)–C(6′)	119.1(14)	C(4′)–O(5′)–C(6′)	119.8(15)
O(5′)–C(6′)–O(6′)	120.5(18)	O(5′)–C(6′)–O(6′)	118.6(20)
O(5′)–C(6′)–C(7′)	113.5(16)	O(5′)–C(6′)–C(7′)	116.2(18)
O(6′)–C(6′)–C(7′)	126.1(20)	O(6′)–C(6′)–C(7′)	124.9(23)
C(1′)–N(8′)–N(9′)	120.5(12)	C(1′)–N(8′)–N(9′)	120.0(12)
N(8′)–N(9′)–C(10′)	119.1(12)	N(8′)–N(9′)–C(10′)	119.3(12)
N(9′)–C(10′)–C(11′)	120.7(16)	N(9′)–C(10′)–C(11′)	121.1(16)
N(9′)–C(10′)–C(15′)	117.4(14)	N(9′)–C(10′)–C(15′)	115.4(14)
C(11′)–C(10′)–C(15′)	121.9(14)	C(11′)–C(10′)–C(15′)	123.5(15)
C(10′)–C(11′)–C(12′)	117.7(19)	C(10′)–C(11′)–C(12′)	117.1(17)
C(11′)–C(12′)–C(13′)	120.7(18)	C(11′)–C(12′)–C(13′)	121.8(16)
C(12′)–C(13′)–C(14′)	120.1(17)	C(12′)–C(13′)–C(14′)	119.0(18)
C(13′)–C(14′)–C(15′)	119.9(18)	C(13′)–C(14′)–C(15′)	123.1(21)
C(10′)–C(15′)–C(14′)	119.6(15)	C(10′)–C(15′)–C(14′)	115.3(16)
C(2′)–O(16′)–C(17′)	116.9(11)	C(2′)–O(16′)–C(17′)	115.0(11)
O(16′)–C(17′)–O(17′)	124.7(14)	O(16′)–C(17′)–O(17′)	122.1(13)
O(16′)–C(17′)–C(18′)	109.7(13)	O(16′)–C(17′)–C(18′)	111.9(14)
O(17′)–C(17′)–C(18′)	125.5(15)	O(17′)–C(17′)–C(18′)	126.0(16)
C(3′)–O(19′)–C(20′)	118.4(10)	C(3′)–O(19′)–C(20′)	118.1(11)
O(19′)–C(20′)–O(20′)	122.4(13)	O(19′)–C(20′)–O(20′)	122.1(14)
O(19′)–C(20′)–C(21′)	114.1(13)	O(19′)–C(20′)–C(21′)	110.3(13)
O(20′)–C(20′)–C(21′)	123.5(16)	O(20′)–C(20′)–C(21′)	127.6(17)

surprising and the reaction mechanism could be discussed in terms of the reactivity of the carbonyl groups of the furantrione (**6**) (C-3 > C-4 > C-2) and could be pictured as shown in Scheme 3. The reaction will proceed *via* initial nucleophilic attack of one of the NH_2 groups of the diamine on the C-3 carbonyl of (**6**) and loss of a water molecule, followed by intramolecular nucleophilic attack by the other NH_2 group of the diamine on the second-most active carbonyl group C-4 of (**6**) to afford the intermediate **I**. This will be the major possibility in the absence of other competing nucleophiles (*e.g.*, hydrazine). The experiments have confirmed our expectation and the product (**10**) was found to be the major product when compound (**6**) was allowed to react with the diamine for a longer time before the arylhydrazine was added.

Experimental

M.p.s were determined on a Mel-Temp melting point apparatus and are uncorrected. Analytical TLC was performed using an ascending technique with EM silica gel 60 F_{254} precoated on plastic sheets. IR spectra were obtained on a Perkin-Elmer model 599 spectrometer and were calibrated against the 1 601 cm^{-1} band of polystyrene. ^1H NMR spectra were recorded on IBM NR-80, Varian EM-390, or Nicolet NMC 300 MHz spectrometers. Chemical shifts are expressed in δ-units (ppm) downfield from internal tetramethylsilane (Me_4Si). The ^{13}C NMR spectrum of (**3**) was obtained using a Bruker AMX-400 spectrometer. A Hewlett-Packard 5995 gas chromatograph/mass spectrometer was used to record mass spectral data at 70 eV. X-Ray data were recorded on a Nicolet R3m diffractometer and were analysed on a MicroVAX II using the SHELXTL PLUS series of crystallographic programs. Elemental analyses were performed at Alexandria University, Faculty of Science Central Laboratory and at M-H-W Laboratories, Phoenix, Arizona. Compound (**1**) was synthesized as previously reported.[3]



Scheme 3. i, *o*-phenylenediamine; ii, $ArNHNH_2$.

3-[L-threo-2,3,4-*Tri*-O-*acetoxy*-1-*phenylhydrazonobutyl*]-*quinoxaline*-2(1H)-*one* (**3**) *hemihydrate*.—A solution of compound (**1**) (3.54 g, 10 mmol) in pyridine (50 ml) was treated with acetic anhydride (8 ml) and the mixture was kept at room temperature for 2 days. The reaction mixture was then poured onto crushed ice, and the *title product* that separated out was filtered off, washed repeatedly with water, and dried. It was recrystallized from chloroform–methanol in the cold (3.9 g, 80%), m.p. 136–138 °C (Found: C, 58.9; H, 5.4; N, 11.2. $C_{24}H_{24}N_4O_7 \cdot 0.5H_2O$ requires C, 58.89; H, 5.15; N, 11.45%); $\delta_H(CDCl_3)$ 2.05, 2.06, and 2.15 (3 s, 9 H, 3 × Ac), 2.67 (br s, 1 H, 0.5 H_2O), 4.55 (2 q, $J_{3,4} \sim 3.8$, $J_{3,4'} \sim 3.4$, and $J_{4,4'} \sim 12.0$ Hz, 2 H, butyl 4-H_2), 6.05 (m, 1 H, butyl 3-H), 7.00–7.61 (m, 10 H, butyl 2-H and ArH), 12.31 (s, 1 H, =NNH), and 14.42 (s, 1 H, NHCO); $\delta_C(CDCl_3)$ 20.85, 21.04, 21.18, 63.41, 71.92, 71.94, 114.47, 115.70, 122.86, 124.66, 127.84, 128.35, 129.50, 130.68, 130.96, 131.28, 143.41, 148.84, 155.91, 170.61, 170.66, and 170.89.

3-[1-(*Arylhydrazono*)*ethyl*-2-*hydroxy*-2-*phenyl*]*quinoxalin*-2(1H)-*ones* (**7**).—*General procedure*. A solution of compound (**6**) (0.01 mol) in methanol (10 ml) was treated with a solution of *o*-phenylenediamine (0.01 mol) in a mixture of methanol (10 ml) and water (60 ml), the mixture was boiled for 1–2 min, and the respective arylhydrazine (0.01 mol) was then added. The mixture was boiled under reflux for 10 min, and the respective product that separated was recrystallized from ethanol, to give red needles. Thus were prepared the following compounds.

3-[2-*Hydroxy*-2-*phenyl*-1-(*phenylhydrazono*)*ethyl*]*quinoxalin*-2(1H)-*one* (**7a**). Yield 68%; m.p. 194–197 °C (lit.,[7] 195 °C); $\delta_H[(CD_3)_2SO]$ 5.73 (d, $J \sim 7$ Hz, 0.6 H, OH form A), 5.90 (d, $J \sim 7$ Hz, 0.6 H, CH form A), 6.6–8.00 (m, 14.8 H, ArH and CHOH of form B), 10.47 (s, 0.6 H, =NNH), 10.63 [s, 0.4 H, N(4)–H], and 11.47 [s, 1 H, N(1)–H]; *m/z* 370 ($M^{\cdot+}$, 0.29%), 368 ($M^{\cdot+} - 2$, 1.49), 352 ($M^{\cdot+} - 18$, 78), 261 (39), 247 (55), 232 (15), 180 (100), 171 (83), and 116 (78).

3-[1-(p-*Bromophenylhydrazono*)-2-*hydroxy*-2-*phenylethyl*]-*quinoxalin*-2(1H)-*one* (**7b**). Yield 71%; m.p. 202–205 °C (Found: C, 58.8; H, 3.75; N, 12.3. $C_{22}H_{17}BrN_4O_2$ requires C, 58.81; H, 3.82; N, 12.47%); $\delta_H[(CD_3)_2SO]$ 5.68 (d, $J \sim 5.9$ Hz, 0.78 H, OH form A), 5.86 (d, $J \sim 5.9$ Hz, 0.78 H, CH form A), 6.42–7.85 (m, 13.44 H, ArH and CHOH of form B), 10.35 (s, 0.78 H, =NNH), 10.76 [s, 0.22 H, N(4)–H], and 12.43 [s, 1 H, N(1)–H].

3-[1-(p-*Chlorophenylhydrazono*)-2-*hydroxy*-2-*phenylethyl*]-*quinoxalin*-2(1H)-*one* (**7c**). Yield 73%; m.p. 204–206 °C (Found: C, 65.1; H, 4.1; N, 13.9. $C_{22}H_{17}ClN_4O_2$ requires C, 65.27; H, 4.23; N, 13.84%); $\delta_H[(CD_3)_2SO]$ 5.60 (d, $J \sim 6.0$ Hz, 0.8 H, OH form A), 5.85 (d, $J \sim 6.0$ Hz, 0.8 H, CH form A), 6.75–7.83 (m, 13.4 H, ArH and CHOH of form B), 10.33 (s, 0.8 H, =NNH), 10.70 [s, 0.2 H, N(4)–H], and 12.40 [s, 1 H, N(1)–H].

3-*Arylhydrazono*-2,3-*dihydro*-2-*phenylfuro*[2,3-b]*quinoxalines* (**8**).—*General procedures*. (*a*) A solution of compound (**7**) (1 mmol) in pyridine (3 ml) was treated with acetic anhydride (0.5 ml) at room temperature and the mixture was stirred for 2 h, and then left overnight. The reaction mixture was poured onto crushed ice. Filtration and recrystallization from ethanol gave the furoquinoxaline (**8**) as reddish-orange needles.

(*b*) A solution of compound (**7**) (1 mmol) in acetic anhydride (5 ml) was boiled under reflux for 2 h, then cooled and poured onto crushed ice. The product was identical with that obtained from method (*a*). The following compounds were thus prepared.

2,3-*Dihydro*-2-*phenyl*-3-*phenylhydrazonofuro*[2,3-b]*quinoxaline* (**8a**). Yield 80% [method (*a*)], 92% [method (*b*)]; m.p. 217–219 °C (Found: C, 75.1; H, 4.6; N, 16.0. $C_{22}H_{16}N_4O$ requires C, 74.98; H, 4.58; N, 15.90%); $\delta_H[(CD_3)_2SO]$ 6.70 and 6.90 (~2:1) (2 s, 1 H, CH), 7.52 (m, 14 H, ArH), and 10.12 and 11.50 (2 s, ~1:2, 1 H, NH); *m/z* 352 (M^+, 41%), 261 (11), 247 (21), 245 (12), 116 (17), 105 (78), and 77 (100).

3-(p-*Bromophenylhydrazono*)-2,3-*dihydro*-2-*phenylfuro*[2,3-b]*quinoxaline* (**8b**). Yield 90% [method (*b*)]; m.p. 206–208 °C (Found: C, 60.9; H, 3.4; N, 12.8. $C_{22}H_{15}BrN_4O$ requires C, 61.25; H, 3.51; N, 12.99%); $\delta_H[(CD_3)_2SO]$ 6.67 and 6.77 (2 s, ~2:1, 1 H, CH), 6.77–8.42 (m, 13 H, ArH), and 10.15 and 12.09 (2 s, ~1:2, 1 H, NH); *m/z* 430 and 432 ($M^{\cdot+}$, $M^{\cdot+} + 2$, 100 and 100%), 247 (47), 219 (32), 218 (25), 185 (52), 183 (52), 172 (16), 170 (15), 169 (57), 157 (74), 155 (87), 145 (10), 143 (11), and 105 (41).

3-(p-*Chlorophenylhydrazono*)-2,3-*dihydro*-2-*phenylfuro*[2,3-b]*quinoxaline* (**8c**). Yield 91% [method (*b*)]; m.p. 202–204 °C (Found: C, 67.9; H, 3.8; N, 14.2. $C_{22}H_{15}ClN_4O$ requires C, 68.31; H, 3.91; N, 14.49%); $\delta_H[(CD_3)_2SO]$ 6.60 and 6.75 (2 s, ~3:1, 1 H, CH), 7.0–8.3 (m, 13 H, ArH), and 10.17 and 12.03 (2 s, ~1:3, 1 H, NH); *m/z* 386 and 388 ($M^{\cdot+}$, $M^{\cdot+} + 2$, 100 and 35%), 247 (60), 219 (31), 218 (24), 141 (23), 139 (58), 113 (33), and 111 (98).

Action of Sodium Hydroxide on Compounds (**8**).—*General procedure*. Compound (**8**) (1 mmol) was dissolved in a solution of sodium hydroxide (0.49, 10 mmol) in 1:1 water–ethanol (10 ml). The mixture boiled under reflux for 2 h, cooled, and acidified with acetic acid, and the product that separated out was removed by filtration, washed with water, and dried. Recrystallization of the product from ethanol afforded the hydrazono alcohols (**7**) as reddish-orange needles in 70–76% yield.

Isolation and characterization of compounds (**10**). These were isolated from the mother liquor from the preparation of compounds (**7**) in 10–15% yield, as follows.

Hydrazide (**10a**) had m.p. 183 °C (Found: C, 71.5; H, 4.75; N, 15.1. $C_{22}H_{18}N_4O_2$ requires C, 71.33; H, 4.90; N, 15.13%);

Table 5. Structure determination summary for compound (3)·0.5H_2O ($C_{24}H_{24}N_4O_7$·0.5H_2O).

Crystal data	
Formula	$C_{24}H_{24}N_4O_7$·0.5H_2O
Colour and habit	red needles
Size (mm)	0.18 × 0.22 × 0.50
Crystal system	monoclinic
Space group	$P2_1$ (No. 4)
Unit-cell dimensions	*a* 16.318(4)
(*a*, *b*, *c* Å)	*b* 17.094(4) β 98.01(2)
(angles °)	*c* 8.906(1)
Volume (Å^3)	2 459.8(9)
Z (formulae/cell)	4
Formula weight	489.53
Density, calc. (g cm^3)	1.32
Absorption coeff. (cm^{-1})	0.93
F(000) (e^-)	1 028
Data collection	
Diffractometer	Nicolet R3m
Radiation	Mo-K_a (λ 0.710 73 Å)
Monochromator	highly oriented graphite crystal
Temperature (K)	294
2θ range (°)	3.0–55.0
h, *k*, *l* limits	0–19, 0–20, −11–11
Scan type	2θ–θ
Scan speed (° min^{-1})	variable; 4.0–29.3
Scan range (°)	0.8 on either side of $K_{\alpha 12}$
Background measurement	stationary crystal and counter at beginning and end of scan; total background time: scan time ratio 0.5
Standard reflections	3 measured every 37
Reflections collected	5 939 total; 5 742 independent; *R*(int) 0.0336
Reflections observed	2 204; $F > 6\sigma(F)$
Absorption correction	not applied
Min/max transmission	not applied
Solution and refinement	
System used	Nicolet SHELXTL PLUS (MicroVAX II)
Solution	direct methods (XS:TREF)
Refinement method	full-matrix least-squares (XLS)
Absolute configuration	not applied
Extinction correction	not applied
Final residuals	*R*(*F*) 0.0945 *wR*(*F*) 0.1048
Goodness-of-fit	*S* 3.03
Max and mean |shift/ESD|	0.001 and 0.000
Number of variables	284
Data-to-parameter ratio	7.8:1
Max/min excursions	0.63 and −0.56 e$^-$ A^{-3}

$R(F) = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; $wR(F) = [\Sigma(w\cdot||F_o| - |F_c||^2)/\Sigma w\cdot|F_o|^2]^{\frac{1}{2}}$; $w = [\sigma^2(F) + |g|F^2)]^{-1}$; $g = 0.000\,254$; $s = [\Sigma(w\cdot||F_o| - |F_c|^2)/(M - N)]^{\frac{1}{2}}$ where M is the number of observed reflections, and N is the number of parameters refined.

$\delta_H[(CD_3)_2SO]$ 6.23 (d, 1 H, OH), 6.60 (d, 1 H, CH), 6.68–8.36 (m, 15 H, 14 ArH and NH), and 10.63 (s, 1 H, HNCO); ν_{max}(KBr) 3 401, 3 272, and 1 654 cm^{-1}; *m*/*z* 370 ($M^{\cdot+}$, 2%), 352 ($M^{\cdot+} - H_2O$, 3), and 262 ($M^{\cdot+} - C_6H_8N_2$, 100).

Hydrazide (**10b**) had m.p. 201–202 °C (Found: C, 58.6; H, 3.6; N, 12.5. $C_{22}H_{17}BrN_4O_2$ requires C, 58.81; H, 3.82; N, 12.47%); $\delta_H[(CD_3)_2SO]$ 6.15 (br s, 1 H, OH), 6.51 (br s, 1 H, CH), 6.73, 7.30, and 8.10 (d, m, and m, 14 H, 13 ArH and NH), and 10.65 (s, 1 H, HNCO); ν_{max}(KBr) 3 319, 3 245, and 1 686 cm^{-1}; *m*/*z* 448 and 450 ($M^{\cdot+}$, $M^{\cdot+}$ + 2; 2 and 2%), 430 and 432 (11 and 11), 353 and 355 (12 and 12), 262 (90), and 218 (100).

Hydrazide (**10c**) had m.p. 185–186 °C (Found: C, 65.6; H, 4.2; N, 13.8. $C_{22}H_{17}ClN_4O_2$ requires C, 65.27; H, 4.23; N, 13.84%); $\delta_H[(CD_3)_2SO]$ 6.13 (d, 1 H, OH), 6.53 (d, 1 H, CH), 6.74, 7.30, and 8.00 (d, m, and m, 14 H, 13 ArH and NH), and 10.60 (s, 1 H, HNCO); ν_{max}(KBr) 3 321, 3 240, and 1 680 cm^{-1}; *m*/*z* 386 and 388 ($M^{\cdot+} - H_2O$, $M^{\cdot+}$ + 2 − H_2O, 4 and 1%), 309 and 311 (9 and 2), and 262 (100).

Structure Determination Summary for Compound (**3**)·0.5H_2O ($C_{24}H_{24}N_4O_7$·0.5H_2O).—See Table 5.

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