Crystal and Molecular Structures of Sydnones, 4,5-Diphenylisosydnone, and Mesoionic Tetrazoles

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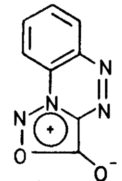
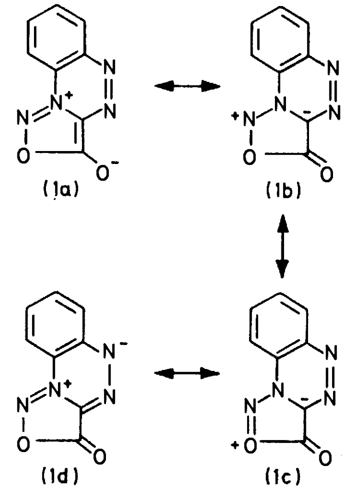
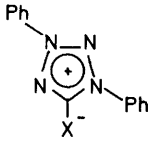
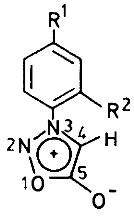
The crystal and molecular structures of 3-(2-aminophenyl)sydnone (3b), [1,2,3]oxadiazolo[4,3-*c*][1,2,4]benzotriazinium-3-olate (1), 4,5-diphenylisosydnone (6), 1,3-diphenyltetrazolium-5-thiolate (2a), and 2,3-diphenyltetrazolium-5-olate (10b) have been determined *X*-ray crystallographically. The molecular parameters of the sydnone derivatives and of (6) are in accord with open-chain structures rather than with a conventional mesoionic formulation. The C–S bond length of (2a) is very close to the reported value for the isomeric dehydrodithizone whilst the C–O distance in (10b) is in the region normally observed in amides.

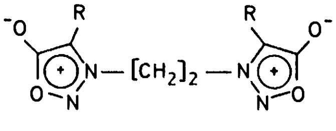
RECENTLY we described[1] the synthesis of [1,2,3]oxadiazolo[4,3-*c*][1,2,4]benzotriazinium-3-olate (1) and of a new mesoionic tetrazole (2a).[2] In this paper we discuss the crystal and molecular structures of these and related derivatives.


(1)


(1a) (1b) (1c) (1d)

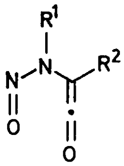

(2) a; X = S
b; X = O


(3) a; R^1 = Br, R^2 = H
b; R^1 = H, R^2 = NH_2


(4) a; R = H
b; R = Cl

Sydnones and 4,5-Diphenylisosydnone

Two *X*-ray crystallographic studies of sydnones have been reported but isosydnones have not been investigated in this context. Bärnighausen *et al.*[3] noted that the exocyclic C–O distance (1.20 Å) of *p*-bromophenyl sydnone (3a) was in accord with a C=O double bond (*cf.* 1.19—1.22 Å in simple carbonyl compounds and 1.21—1.27 Å in amides). A severe bond-angle distortion about the carbonyl group [C–C–O(exocyclic) 135.7°] was ascribed to an intramolecular charge-transfer interaction between a bromine of one molecule and a neighbouring carbonyl oxygen. From a subsequent, more detailed study[4] of bis-sydnones (4), three important features have emerged (*cf.* 4b): (i) the ring distances except that of the endocyclic C–O bond are midway between single and double bond (*i.e.* C–C 1.406 Å, *cf.* benzene 1.397 Å;[5] C–N 1.335 Å, *cf.* pyridine 1.340 Å;[6] N–N 1.316 Å, *cf.* tetrazine 1.321 Å;[7] N–O 1.382 Å, *cf.* 1,2,5-oxadiazole 1.380 Å[8]); (ii) the C–O ring distance (1.406 Å) is long [*cf.* furan 1.362 Å (ref. 9) and anemonin 1.37 Å (ref. 10)]; (iii) a distortion of the C–C–O(exocyclic) bond angle (135.5°) is evident.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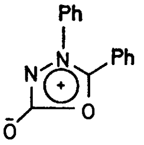

(6)

These observations have led to the suggestion[4] that the valence tautomeric nitroso-ketene (5) makes a substantial contribution to the syndone structure.

The molecular structure of [1,2,3]oxadiazolo[4,3-*c*]-[1,2,4]benzotriazinium-3-olate (1) appeared to present additional features of interest. Representation by structure (1) implies a conventional mesoionic formulation in which a sydnone ring is condensed with a benzo-1,2,4-triazine [*cf.* canonical forms (1a)—(1c)]. On the other hand canonical form (1d) represents an oxadiazole condensed with a benzotriazinium betaine. A crystallographic comparison of this material (1) with 3-(*o*-aminophenyl)sydnone (3b) as a model compound was therefore desirable, whilst a general comparison of sydnones with isosydnones was of interest.

EXPERIMENTAL

X-*Ray Structure Determinations*.—All parameters were first determined by oscillation and Weissenberg photographs and then refined by least-squares from the setting angles of 23 reflections on a Hilger and Watts four-circle diffractometer.

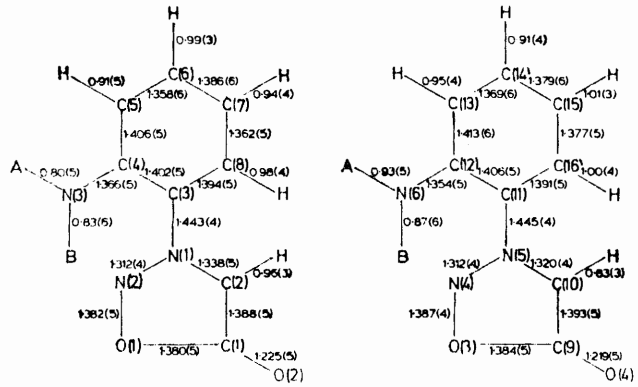


FIGURE 1 Bond lengths (Å) in 3-(2-aminophenyl)sydnone (3b)

In all cases reflections were scanned (ω—2θ mode) out to 25° using Mo-K_α radiation (graphite monochromator). Reflections were deemed observed if the net count was $>3\sigma(I)$; Lorentz and polarization but not absorption corrections were made.

The three structures were routinely solved by use of MULTAN [11] and were refined by least-squares, using full matrix for the tricyclic compound, refining in four blocks for the bicyclic compound, and in two blocks for the isosydnone. During the later stages of refinement hydrogen atoms, found from difference maps, were included and refined isotropically for the sydnones and left in fixed positions for the isosydnone, the other atoms refining anisotropically. A weighting scheme of the form $W = 1/\{1 + [(F_o - A)/B]^2\}$ was applied in the case of the sydnones, and for the isosydnone the weighting scheme employed a fourth-order Chebyshev series in $T_1(X)$ where $X = F_o/F_o(\text{max.})$, the four values for the coefficients being 320.1, 474.49, 183.3, and 26.8.

TABLE 1

3-(2-Aminophenyl)sydnone (3b): fractional co-ordinates ($\times 10^4$, for H $\times 10^3$) with standard deviations in parentheses. Hydrogens are numbered according to the atom to which they are attached

Atom	*x*/*a*	*y*/*b*	*z*/*c*
N(1)	3 638(1)	9 622(9)	169(1)
N(2)	3 262(2)	10 517(12)	−370(1)
N(3)	2 312(2)	12 853(14)	300(2)
O(1)	3 618(1)	9 257(10)	−849(1)
O(2)	4 591(1)	6 289(11)	−935(1)
C(1)	4 209(2)	7 614(12)	−585(2)
C(2)	4 204(2)	7 880(12)	79(2)
C(3)	3 414(2)	10 533(10)	779(1)
C(4)	2 775(2)	12 016(11)	819(2)
C(5)	2 622(2)	12 760(12)	1 445(2)
C(6)	3 061(2)	12 055(12)	1 984(2)
C(7)	3 686(2)	10 531(12)	1 931(2)
C(8)	3 863(2)	9 815(12)	1 335(2)
H(C2)	451(2)	695(10)	432(2)
H(C5)	222(2)	1 382(13)	147(2)
H(C6)	295(1)	1 275(9)	242(2)
H(C7)	398(2)	1 013(10)	231(2)
H(C8)	427(2)	851(12)	127(2)
H(N3A)	205(2)	1 940(13)	33(2)
H(N3B)	239(3)	1 198(18)	−5(3)
N(4)	4 511(1)	5 293(12)	3 296(1)
N(5)	5 098(1)	4 745(9)	3 648(1)
N(6)	5 246(2)	5 166(12)	2 273(2)
O(3)	4 048(1)	3 789(9)	3 658(1)
O(4)	4 045(1)	975(9)	4 613(1)
C(9)	4 371(2)	2 422(12)	4 232(2)
C(10)	5 055(2)	3 137(12)	4 203(2)
C(11)	5 709(2)	5 961(10)	3 410(2)
C(12)	5 754(2)	6 046(11)	2 742(2)
C(13)	6 382(2)	7 208(13)	2 570(2)
C(14)	6 909(2)	8 161(13)	3 026(2)
C(15)	6 852(2)	8 015(13)	3 678(2)
C(16)	6 248(2)	6 922(12)	3 870(2)
H(C10)	539(2)	258(9)	446(2)
H(C13)	624(2)	750(12)	212(2)
H(C14)	729(2)	896(12)	287(2)
H(C15)	722(2)	904(10)	400(2)
H(C16)	619(2)	712(11)	434(2)
H(N6A)	534(2)	433(12)	188(2)
H(N6B)	485(3)	467(16)	240(3)

(a) 3-(2-*Aminophenyl*)*sydnone* (3b). *Crystal data.* $C_8H_7N_3O_2$, $M = 177.1$, Monoclinic $a = 15.284(2)$, $b = 3.802(2)$, $c = 26.898(3)$ Å, $\beta = 92.82(2)°$, $U = 1\,561.8$ Å^3, $D_c = 1.507$ g cm^{-3}, $Z = 8$, $D_m = 1.48$ g cm^{-1}, $F(000) = 736$. Space group $P2_1/n$ from systematic absences. Mo-K_α radiation, $\lambda = 0.710\,69$ Å; $\mu(\text{Mo-}K_\alpha) = 1.22$ cm^{-1}.

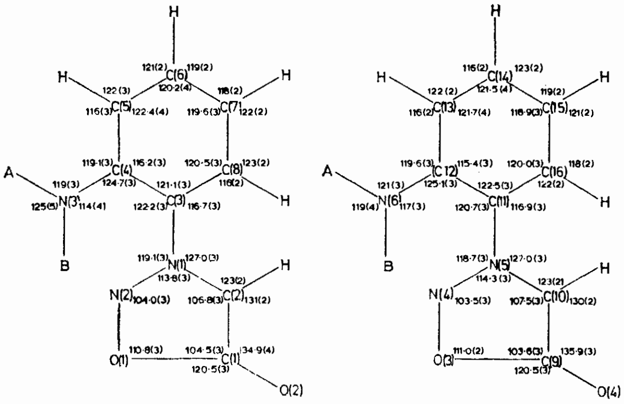


FIGURE 2 Bond angles (°) in 3-(2-aminophenyl)sydnone (3b)

Observable reflections 2 787, observed 1 517; weighting scheme parameters: *A* 12.0, *B* 12.0; final conventional *R* 6.2%.

There is evidence of weak hydrogen bonding between each carbonyl oxygen atom and one of the amine hydrogen atoms of the other independent molecule. Thus H(N3A) · · · O(4) is 2.26 Å and H(N6A) · · · O(2) is 2.00 Å.

Table 1 shows the fractional co-ordinates of the atoms, Figures 1 and 2 show the bond lengths and angles, and Figure 3 is a perspective drawing of the more twisted molecule.

(b) [1,2,3]*Oxadiazolo*[4,3-c][1,2,4]*benzotriazinium*-3-*olate* (1). *Crystal data.* $C_8H_4N_4O_2$, $M = 188.1$, Orthorhombic, $a = 18.682(2)$, $b = 9.593(2)$, $c = 8.561(2)$ Å, $U = 1\,529.5$ Å^3, $D_c = 1.634$ g cm^3, $Z = 8$ $D_m = 1.60$ g cm^3, $F(000) =$

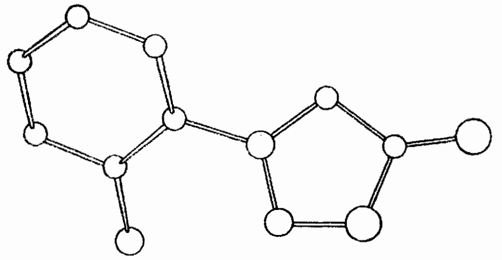


FIGURE 3 Perspective drawing of 3-(2-aminophenyl)sydnone (3b)

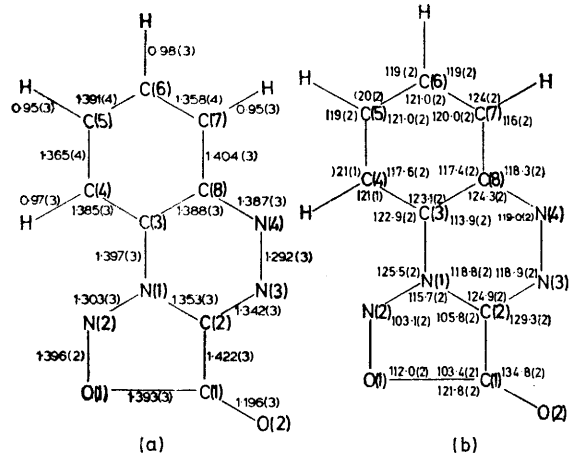


FIGURE 4 [1,2,3]Oxadiazolo[4,3-*c*][1,2,4]benzotriazinium-3-olate (1): (a) bond lengths and (b) angles (°)

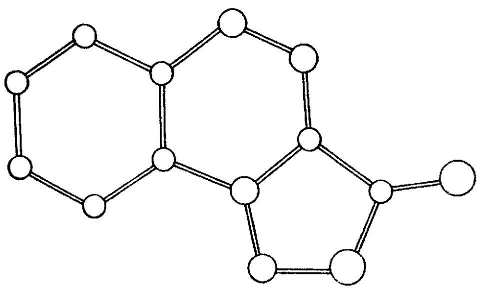


FIGURE 5 Perspective drawing of [1,2,3]oxadiazolo[4,3-*c*]-[1,2,4]benzotriazinium-3-olate (1)

768. Space group *Pbca* from systematic absences. μ(Mo-K_α) = 1.33 cm^{-1}.

Observable reflections 1 347, observed 887; weighting-scheme parameters: *A* 12.0, *B* 15.0; final conventional *R* 3.4%.

Table 2 shows the fractional co-ordinates of the atoms, Figure 4 shows the bond lengths and angles, and Figure 5 is a perspective drawing of the molecule.

TABLE 2

[1,2,3]Oxadiazolo[4,3-*c*][1,2,4]benzotriazinium-3-olate (1): fractional co-ordinates ($\times 10^4$, for H $\times 10^3$) with standard deviations in parentheses. Hydrogens are numbered according to the atom to which they are attached

Atom	*x*/*a*	*y*/*b*	*z*/*c*
N(1)	7 468(1)	9 306(2)	3 307(2)
N(2)	7 786(1)	10 215(2)	2 411(2)
N(3)	7 683(1)	7 399(2)	5 094(2)
N(4)	7 004(1)	7 176(2)	5 190(2)
O(1)	8 512(1)	9 932(2)	2 653(2)
O(2)	9 200(1)	8 493(2)	4 121(2)
C(1)	8 615(1)	8 853(3)	3 722(3)
C(2)	7 905(1)	8 438(2)	4 109(2)
C(3)	6 728(1)	9 165(2)	3 485(3)
C(4)	6 239(1)	10 050(3)	2 774(3)
C(5)	5 529(1)	9 777(3)	2 993(3)
C(6)	5 307(1)	8 650(3)	3 897(3)
C(7)	5 790(1)	7 802(3)	4 608(3)
C(8)	6 526(1)	8 055(2)	4 432(2)
H(C4)	636(2)	1 084(3)	215(3)
H(C5)	519(1)	1 037(3)	251(3)
H(C6)	479(2)	842(3)	396(3)
H(C7)	566(1)	703(3)	524(3)

TABLE 3

4,5-Diphenylisosydnone (6); fractional co-ordinates ($\times 10^4$) with standard deviations in parentheses

Atom	*x*/*a*	*y*/*b*	*z*/*c*
O(1)	18 903(9)	2 243(2)	4 265(1)
O(2)	1 895(1)	1 739(3)	4 913(2)
N(3)	1 948(1)	2 760(3)	5 410(2)
N(4)	1 973(1)	4 004(3)	5 096(2)
C(5)	1 935(1)	3 715(4)	4 376(3)
O(6)	1 938(1)	4 440(3)	3 866(2)
C(7)	1 819(1)	282(3)	4 958(2)
C(8)	1 599(1)	−206(4)	5 341(2)
C(9)	1 527(2)	−1 599(4)	5 363(3)
C(10)	1 668(1)	−2 510(4)	4 987(2)
C(11)	1 880(2)	−2 023(4)	4 594(3)
C(12)	1 961(1)	−633(4)	4 577(2)
C(13)	2 025(1)	2 746(4)	6 234(2)
C(14)	2 373(1)	1 885(4)	6 853(2)
C(15)	2 456(2)	1 955(5)	7 647(2)
C(16)	2 203(2)	2 867(3)	7 815(2)
C(17)	1 858(2)	3 703(4)	7 187(3)
C(18)	1 783(1)	3 651(4)	6 384(2)
O(21)	4 454(1)	852(2)	3 230(2)
C(22)	4 349(1)	−445(3)	2 973(2)
N(23)	4 270(1)	−1 096(3)	3 483(2)
N(24)	4 324(1)	−259(3)	4 121(2)
C(25)	4 438(1)	958(4)	3 968(2)
O(26)	4 515(1)	2 066(3)	4 310(2)
C(27)	4 347(1)	−880(4)	2 249(2)
C(28)	4 363(1)	−2 249(4)	2 059(2)
C(29)	4 372(2)	−2 577(5)	1 359(3)
C(30)	4 364(2)	−1 566(5)	853(3)
C(31)	4 352(2)	−211(5)	1 043(3)
C(32)	4 343(2)	135(4)	1 727(3)
C(33)	4 123(1)	−2 493(4)	3 451(2)
C(34)	3 671(1)	−2 891(4)	2 793(2)
C(35)	3 532(2)	| 4 240(5)	2 759(3)
C(36)	3 846(2)	−5 149(4)	3 384(3)
C(37)	4 437(1)	−3 368(4)	4 094(2)
C(38)	4 437(1)	−3 368(4)	4 094(2)
C(51)	4 718(6)	3 822(6)	278(1)
C(52)	5 187(7)	3 818(6)	3 319(5)
C(53)	5 475(2)	3 834(7)	305(1)

(*c*) 4,5-*Diphenylisosydnone* (6) (*ref.* 12). *Crystal data.* $C_{14}H_{10}N_2O_2\cdot\frac{1}{4}C_6H_6$, *M* = 253.7, Monoclinic, *a* = 33.300, *b* = 9.732(2), *c* = 19.096(3) Å, β = 123.92(2)°, *U* = 5 135.1 Å^3, D_c = 1.312 g cm^{-3}, *Z* = 16, D_m = 1.30 g cm^{-3}, *F*(000) = 2 152. Space group *C*2/*c*. μ(Mo-K_α) = 0.97 cm^{-1}.

Of 4 507 unique reflections scanned, 2 410 were considered observed. Final conventional *R* 5.3%.

Table 3 lists the fractional co-ordinates, Figure 6 shows the bond lengths, Figure 7 the bond angles, and Table 4 selected torsion angles. Figure 8 is a perspective drawing

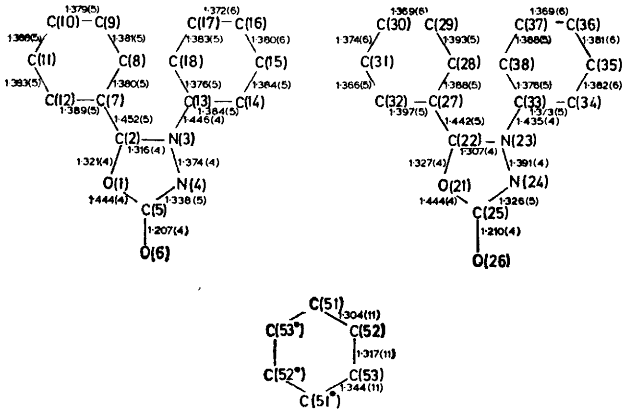


FIGURE 6 Bond lengths (Å) in 4,5-diphenylisosydnone (6)

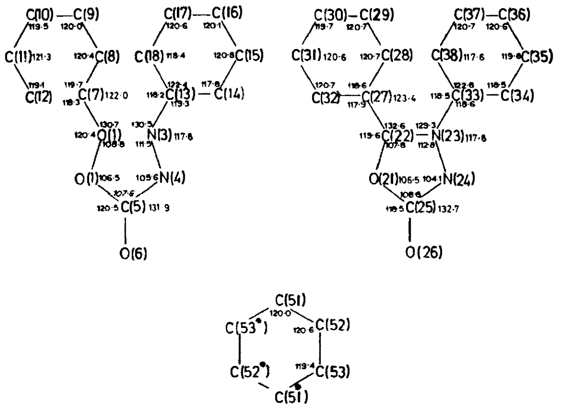


FIGURE 7 Bond angles (°) in 4,5-Diphenylisosydnone (6); standard deviations 0.3 or 0.4° except for solvate where they were 0.7°

of the higher-numbered isosydnone molecule drawn with the heterocyclic ring in the plane of the paper.

Apart from MULTAN,[11] all computations were carried out by use of the *X*-RAY '70 program system [1] for the sydnones and the Oxford CRYSTALS package for the isosydnone.

TABLE 4

4,5-Diphenylisosydnone (6): selected torsion angles (°)

Angle	Molecule (1)	Molecule (2)
C(7)-C(2)-N(3)-C(13)	11.1	−4.0
O(1)-C(2)-C(7)-C(8)	−148.5	163.5
O(1)-C(2)-C(7)-C(12)	29.4	−14.8
N(3)-C(2)-C(7)-C(8)	27.1	−15.7
N(3)-C(2)-C(7)-C(12)	−155.0	166.1
C(2)-N(3)-C(13)-C(14)	47.6	−66.2
C(2)-N(3)-C(13)-C(18)	−135.8	115.6
N(H)-N(3)-C(13)-C(14)	−125.9	111.4
N(H)-N(3)-C(13)-C(18)	50.6	−66.9

Tables of thermal parameters and listings of the observed and calculated structure factors for all the compounds [except for the structure factors for compound (6)] are available in Supplementary Publication No. SUP 22576 (41 pp.).*

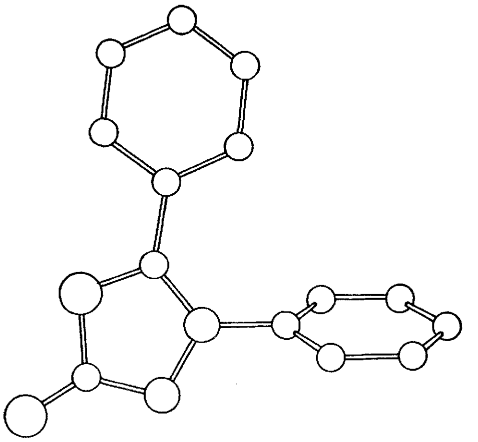
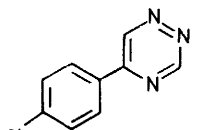


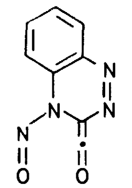
FIGURE 8 Perspective drawing of the higher-numbered 4,5-diphenylisosydnone molecule (6)

DISCUSSION

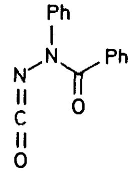
The bond angles and lengths of the independent 3-(2-aminophenyl)sydnone molecules (Figures 1 and 2) are in agreement. Bond-distance values are very close to those of Thiessen and Hope for the bis-sydnone (4b),[4] although the C–O ring distance is slightly shorter. An additional feature is the difference in dihedral angle between the aryl and sydnone rings which in one case is 6° and in the other 30°. Bärnighausen *et al.*[3] noted a corresponding dihedral angle of 27.6° in *p*-bromophenylsydnone (3a) which they ascribed to steric repulsion of an *ortho*-hydrogen with the sydnone H(C4) atom. Clearly the amino-derivative (3b) adopts a configuration in which such an *ortho*-interaction is minimised, *i.e.* the amino-group is directed away from atom H(C4). The severe bond-angle distortion about the carbonyl group is again apparent (see Figure 2) hence this compound (3b) is structurally similar to (3a) [3] and (4b) [4] [*cf.* (5)].[4]



(7)



(8)



(9)

[1,2,3]Oxadiazolo[4,3-*c*][1,2,4]benzotriazinium-3-olate (1) [1] is essentially planar and exhibits some similar structural properties to those already mentioned, *viz.* the C(1)–O(1) bond is relatively long, the C(1)–O(2) bond is almost of double-bond character, and there is a marked deformation of bond angles around C(1). Interestingly the N(3)–N(4) distance (1.292 Å) is considerably shorter than the N(1)–N(2) bond (1.335 Å) of the related 1,2,4-triazine derivative (7) [14] whilst the C(2)–N(3) bond (1.342 Å) is nearer to a single bond than the corresponding bond in (7) (1.314 Å). It can be concluded that the contribution of the canonical form (1d) to the overall resonance hybrid is unimportant. On the evidence available it would appear that a keten type of structure (8) contributes substantially to the overall bonding situation in this case also.

In both independent 4,5-diphenylisosydnone molecules the dimensions are very similar and the individual rings are essentially planar. The phenyl carbon atoms attached to the heterocyclic rings are significantly displaced one up and one down from the plane of the ring, and both phenyl rings are appreciably twisted out of coplanarity with it. The magnitudes of these distortions are most clearly indicated by reference to Table 4.

The bond-angle distortion about the carbonyl group is again apparent (see Figure 6) and the O(1)–C(5) ring distance is long compared to the analogous bond in sydnones [*cf.* (1), (3a, b)]. Evidently an open-chain formulation [*cf.* (9)] is also important in describing the diphenylisosydnone structure.

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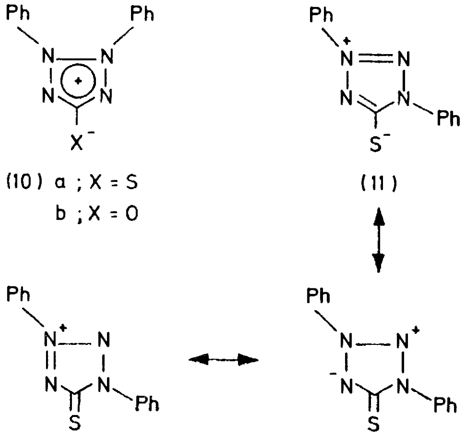
* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1978, Index issue.

Mesoionic Tetrazoles

Of the four mesoionic tetrazoles [(2a),[2] (2b),[15] (10a),[16] and (10b) [15]] only dehydrodithizone [17] has been examined X-ray crystallographically. The conventional [16] mesoionic formulation is apparent: the N–N (1.316 Å) and C–N (1.360 Å) ring distances indicate that there are no true single or double bonds in the tetrazole moiety; the C–S distance (1.687 Å) is intermediate between values for a single (1.81 Å) and a double bond (1.56 Å). It can be concluded that there is a high degree of residual negative charge on sulphur.

In the present work it was deemed of interest to attempt a structural comparison of the four mesoionic tetrazole isomers two of which (2a, b) are of type A (ref. 16) and two of type B (10a, b); [16] suitable crystals of (2a) and of (10b) were obtained.



(10) a ; X = S
b ; X = O

(11)

(11b)

(11a)

EXPERIMENTAL

X-ray Structure Determinations.—(*a*) 1,3-*Diphenyltetrazolium-5-thiolate* (2a).[2] Cell parameters were determined and refined as before (crystal mounted about the c axis).

Crystal data. $C_{13}H_{10}N_4S$, $M = 254.2$, Monoclinic, $a = 12.603(3)$, $b = 11.224(3)$, $c = 8.808(3)$ Å, $\beta = 99.4(1)°$, $U = 1\,229.2$ Å^3, $D_c = 1.374$ g cm^{-3}, $Z = 4$, $D_m = 1.37$ g cm^{-3}, $F(000) = 528$. Space group $P2_1/c$ from systematic absences. μ(Mo-K_α) = 2.48 cm^{-1}.

Intensities were measured out to $\theta \leqslant 25°$ and a total of 2 164 observable reflections were scanned (ω—2θ mode) of which 1 458 had a net count of $\geqslant 3\ \sigma$ and were deemed observed. Lorentz and polarisation but not absorption corrections were made.

The structure was solved routinely by use of the centrosymmetric direct-methods program of the SHELX system.[18] Refinement proceeded normally by full-matrix least-squares methods. Hydrogen atoms were located from a difference map and included in the later stages of the refinement with isotropic temperature factors. The weighting scheme parameters were A 30.0 and B 20.0. At convergence (maximum shift of non-hydrogen parameter 0.03 σ) the conventional R was 4.1%.

The individual rings were effectively flat (maximum deviation from the mean plane <0.01 Å). The angles of twist of the phenyl rings relative to the heterocyclic ring were 52° for the ring next to sulphur and 13.5° for the other ring.

TABLE 5

1,3-Diphenyltetrazolium-5-thiolate (2a): fractional co-ordinates (× 10^4, for H × 10^3) with standard deviations in parentheses. Hydrogen atoms are numbered according to the atom to which they are attached

Atom	*x/a*	*y/b*	*z/c*
S(1)	6 704(1)	3 286(1)	−615(1)
C(1)	7 622(2)	2 512(3)	555(3)
N(1)	8 457(2)	2 938(2)	1 563(3)
N(2)	8 935(2)	1 970(2)	2 238(3)
N(3)	8 508(2)	958(2)	1 774(3)
N(4)	7 682(2)	1 280(2)	711(3)
C(2)	6 955(2)	372(3)	23(3)
C(3)	6 560(2)	−427(3)	967(4)
C(4)	5 872(3)	−1 314(3)	326(4)
C(5)	5 591(3)	−1 388(3)	−1 247(4)
C(6)	5 988(3)	−584(3)	−2 178(4)
C(7)	6 682(3)	309(3)	−1 557(4)
C(8)	9 870(2)	2 035(3)	3 406(3)
C(9)	10 151(3)	3 127(3)	4 068(4)
C(10)	11 057(3)	3 187(4)	5 182(4)
C(11)	11 655(3)	2 196(4)	5 609(4)
C(12)	11 367(3)	1 119(4)	4 930(4)
C(13)	10 465(3)	1 031(3)	3 816(4)
H(C3)	677(2)	−34(2)	209(3)
H(C4)	560(3)	−189(3)	100(4)
H(C5)	507(3)	−199(3)	−176(4)
H(C6)	582(3)	−64(3)	−328(4)
H(C7)	693(3)	90(3)	−218(4)
H(C9)	972(3)	379(3)	378(4)
H(C10)	1 121(2)	395(3)	565(3)
H(C11)	1 232(3)	227(3)	636(4)
H(C12)	1 179(3)	43(3)	522(4)
H(C13)	1 021(2)	33(3)	339(3)

Table 5 lists atom fractional co-ordinates. Figures 9 and 10 show the bond lengths and angles and the crystallographic atom numbering. Figure 11 is a perspective drawing [19] of the molecule. Except for the direct methods program all computations were carried out by use of the Oxford CRYSTALS system.[20]

(*b*) 2,3-*Diphenyltetrazolium-5-olate* (10b).[15] Cell parameters were determined as before then refined by least-squares from the setting angles of 18 reflections on a Hilger-Watt four-circle diffractometer (crystal mounted about a).

Crystal data. $C_{13}H_{10}N_4O$, $M = 238.2$, Orthorhombic, $a = 6.454$, $b = 11.406$, $c = 16.132$ Å, $U = 1\,187.5$ Å^3, $D_c = 1.333$ g cm^{-3}, $Z = 4$, $D_m = 1.34$ g cm^{-3}, $F(000) =$

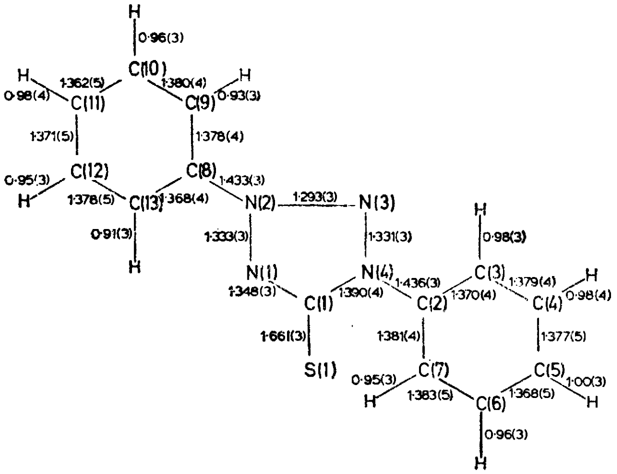


FIGURE 9 Bond lengths (Å) in 1,3-diphenyltetrazolium-5-thiolate (2a)

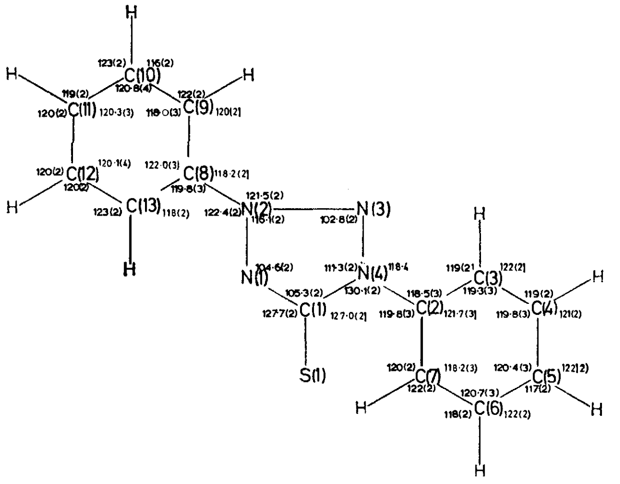


FIGURE 10 Bond angles (°) in 1,3-diphenyltetrazolium-5-thiolate (2a)

496. Space group $P2_12_12_1$ from systematic absences. μ(Mo-K_α) = 0.97 cm^{-1}.

Intensities were measured out to θ 25° and a total of 1 240 observable reflections were scanned (ω—2θ mode) of which 926 had a net count $\geqslant 3\ \sigma$ and were deemed observed. Lorentz polarisation but not absorption corrections were made.

The structure was solved routinely by use of MULTAN.[11] The E map with the highest figure-of-merit revealed the positions of all but two atoms, one in each of the phenyl rings. The position of each of the missing atoms was calculated at the start of the refinement. Refinement proceeded without problems. In the later stages hydrogens (which were first found on a difference map) were included in calculated positions with U 0.05, but not refined, and a weighting scheme of the form W = 1.0 ($A_0 . T_0 . X + A_1$ $T_1 . X + A_2 . T_2 . X + A_3 . T_3 . X$) where A_0 to A_3 are the coefficients for a Chebyshev series in $T(I) . X$ with X = F_0/F_0 (max.), was applied. The coefficients used were A_0 21.55, A_1 23.60, A_2 −0.12, and A_3 −4.32. At convergence

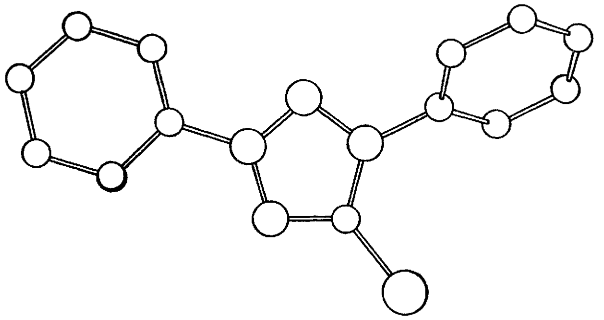


FIGURE 11 Perspective drawing of 1,3-diphenyltetrazolium-5-thiolate (2a)

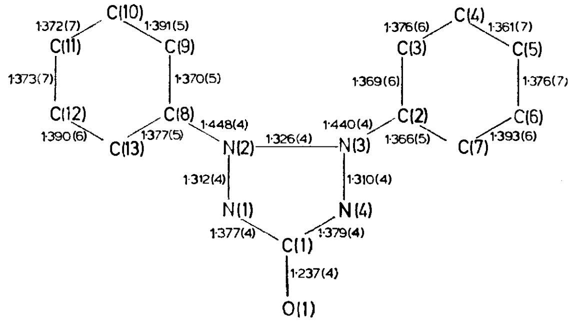


FIGURE 12 Bond lengths (Å) in 2,3-diphenyltetrazolium-5-olate (10b)

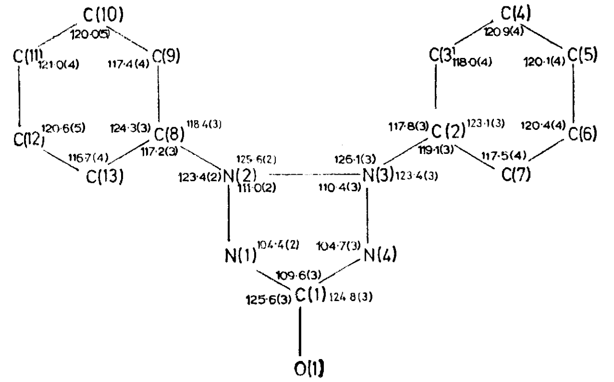


FIGURE 13 Bond angles (°) in 2,3-diphenyltetrazolium-5-olate (10b)

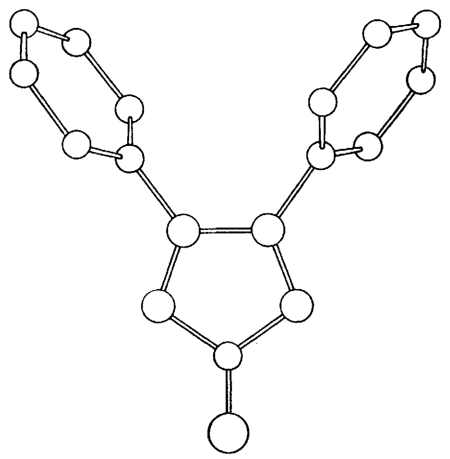


FIGURE 14 Perspective drawing of 2,3-diphenyltetrazolium-5-olate (10b)

TABLE 6

2,3-Diphenyltetrazolium-5-olate (10b): fractional co-ordinates (× 10⁴), with standard deviations in parentheses

Atom	x/a	y/b	z/c
O(1)	529(5)	8 919(2)	299(2)
C(1)	514(6)	7 873(3)	97(2)
N(1)	371(5)	6 939(2)	635(2)
N(2)	401(5)	6 013(2)	152(1)
N(3)	539(5)	6 323(2)	−638(2)
N(4)	630(5)	7 466(2)	−706(2)
C(2)	684(6)	5 539(3)	−1 335(2)
C(3)	2 484(7)	5 545(4)	−1 785(2)
C(4)	2 620(8)	4 809(5)	−2 459(2)
C(5)	1 004(9)	4 108(4)	−2 677(2)
C(6)	−802(9)	4 128(4)	−2 223(3)
C(7)	−987(7)	4 861(4)	−1 537(2)
C(8)	260(6)	4 823(3)	456(2)
C(9)	1 946(7)	4 105(3)	369(2)
C(10)	1 815(9)	2 984(4)	705(3)
C(11)	64(9)	2 647(4)	1 125(3)
C(12)	−1 591(8)	3 394(4)	1 209(3)
C(13)	−1 520(7)	4 518(4)	877(2)

by use of full-matrix anisotropic least-squares the maximum positional shift was 0.13 σ and the conventional R was 4.2%.

The individual rings were effectively flat (maximum deviation from the mean plane <0.01 Å). The phenyl substituents were nearly equally inclined to the heterocyclic ring with angles of twist of 65.4° (low-numbered ring) and 64.4°.

Table 6 lists atom fractional co-ordinates. Figures 12 and 13 show the bond lengths and angles and the crystallographic atom numbering. Figure 14 is a perspective drawing of the molecule. Except for MULTAN,[11] all computations were carried out by use of the Oxford CRYSTALS [20] set of programs.

DISCUSSION

An interesting feature of the structural parameters of the dehydrodithizone isomer (2a) is the similarity in C–S bond length (1.661 Å) which would suggest a similar degree of residual negative charge on the sulphur atom. It can be concluded that the canonical form involving a 1,4-dipolar structure (11) is more significant than alternative 1,3- (11b) or 1,2-dipolar (11c) arrangements; this conclusion is supported by the relatively short N(2)–N(3) (1.293 Å) and C(1)–N(1) (1.348 Å) bonds. The degree of polarization in the analogue (2b) is evidently less marked than in dehydrodithizone. The N–N ring distances are very close to the latter but the C–O bond separation (1.237 Å) is of a magnitude normally observed in amides (1.21—1.27 Å).

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REFERENCES

[1] P. N. Preston and K. Turnbull, *J.C.S. Perkin II*, 1977, 1229.

[2] P. N. Preston, K. K. Tiwari, K. Turnbull, and T. J. King, *J.C.S. Chem. Comm.*, 1976, 343; *cf.* R. N. Hanley, W. D. Ollis, and C. A. Ramsden, *ibid.*, p. 307.

[3] H. Bärnighausen, F. Jellinek, J. Munnik, and A. Vos, *Acta Cryst.*, 1963, **16**, 471.

[4] H. Hope and W. E. Thiessen, *J. Amer. Chem. Soc.*, 1967, **89**, 5977; *Acta Cryst.*, 1969, **B25**, 1237.

[5] A. Langseth and B. P. Stoicheff, *Canad. J. Phys.*, 1956, **34**, 350.

[6] B. Bak, L. Hansen-Nygaard, and J. Hastrup-Anderson, *J. Mol. Spectroscopy*, 1958, **2**, 361.

[7] F. Bertinotti, G. Giacomello, and A. M. Liquori, *Acta Cryst.*, 1956, **9**, 510.

[8] E. Saegebarth and A. P. Cox, *J. Chem. Phys.*, 1975, **43**, 166.

[9] B. Bak, D. Christensen, W. B. Dixon, L. Hansen-Nygaard, J. Hastrup-Andersen, and M. Schottländer, *J. Mol. Spectroscopy*, 1962, **9**, 124.

[10] I. L. Karle and J. Karle, *Acta Cryst.*, 1966, **20**, 555.

[11] G. Germain, P. Main, and M. M. Woolfson, *Acta Cryst.*, 1971, **A27**, 368.

[12] M. Hashimoto and M. Ohta, *Bull. Chem. Soc. Japan*, 1961, **34**, 668.

[13] 1970 Revision of '*X*-RAY '67,' eds. J. M. Stewart, F. A. Kundell, and J. C. Baldwin, University of Maryland Technical Report, 1967, TR 67 58.

[14] J. L. Atwood, D. K. Krass, and W. W. Paudler, *J. Heterocyclic Chem.*, 1974, **11**, 743.

[15] *cf.* P. B. Talukdar, S. K. Sengupta, A. K. Datta, and A. Chakravorty, *Indian J. Chem.*, 1973, **11**, 611 and references therein.

[16] *cf.* W. D. Ollis and C. A. Ramsden, *Adv. Heterocyclic Chem.*, 1976, **19**, 1.

[17] Y. Kushi and Q. Fernando, *J. Amer. Chem. Soc.*, 1970, **92**, 1965.

[18] G. M. Sheldrick, personal communication.

[19] Cambridge Data Centre Program 'PLUTO,' W. D. S. Motherwell, personal communication.

[20] J. R. Carruthers, personal communication.