Dithizone: Redetermination and Refinement of Its Crystal Structure

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Crystals of dithizone are monoclinic, space group $P2_1/n$, $a = 4.70(1)$, $b = 22.25$ (3), $c = 11.95(2)$ Å, $\beta = 98.0(3)°$, $U = 1\ 238$ Å^3, $Z = 4$. The structure was determined from photographic data and refined to R 0.068 for 547 observed data. The molecule is near-planar, of approximate symmetry mm (C_{2v}) with the N–N–C–N–N chain extended and the C–S bond lying on the intersection of the mirror planes. The unique H atoms are bonded to N(1) and N(4). Bond lengths are: S–C 1.71, C–N 1.34, 1.35, N–N 1.29 and 1.30, and N–C(Ph) 1.38 and 1.39 (±0.01) Å. The π-electrons in the N–N–C–N–N system are extensively delocalised. Shortest intermolecular separations are between one molecule and those stacked above and below it parallel to a: N(1) $\cdots$ N(3) (above) 3.38; N(2) $\cdots$ N(4) (above) 3.30 Å: phenyl ring A, attached to N(1), lies directly below N(2) of the molecule above, while phenyl ring B, attached to N(4), lies directly above N(3) of the molecule below.

DITHIZONE ($H_2dz = 1,5$-diphenyl-3-mercaptoformazan) is a well-known reagent in analytical chemistry.[1] It forms stable complexes with many metals, and the crystal structures of several have been reported.[2-8] All show that the bonding to the metal atom involves the sulphur atom and one nitrogen adjacent to a phenyl ring. The crystal structures of several derivatives and related compounds have also been determined: S-methyldithizone,[8,9] a bicyclic oxidation product,[10] diphenylthiocarbazide,[11] dehydrodithizone (a sydnone oxidation product),[12] thiosemicarbazide,[13] (4-phenyl)-thiosemicarbazide,[14] and (1-phenyl)thiosemicarbazide.[15] In all relevant cases, a hydrogen atom is attached to a nitrogen atom to which is bonded a phenyl ring, as was observed in the primary complexes with metals.[3]

Alsop[8] has given a detailed review of the properties of dithizone and has discussed the relationship between the structures of the metal complexes and their i.r. and mass spectra,[16] and there has been a recent i.r. study.[17] The crystal structure of dithizone itself was also reported by Alsop,[8] but it was of lower precision than desirable owing to several circumstances. Crystals of dithizone are very thin laths, elongated along a, susceptible to twinning, and very seldom obtained single. That used by Alsop was twinned, so that the β-angle could not be determined with accuracy and the precision of the intensity measurements was also adversely affected. In spite of these problems, he showed that the molecule was approximately planar with the N–N–C–N–N chain in an extended configuration (and not internally hydrogen-bonded as in the S-methyl derivative [8,9]). He concluded that conjugation along the carbazone chain extended to both phenyl rings. Two possible structures, (Ia) and (Ib), have been suggested and both have received support [(Ia),[10] (Ib) [8,16]].

By good chance, one relatively good single crystal was

obtained from a chloroform solution of dithizone. A redetermination of the structure was therefore undertaken in the hopes of obtaining accurate bonding parameters in the N–N–C(S)–N–N system and, if possible, locating the two hydrogen atoms associated with this system.

(Ia)

(Ib)
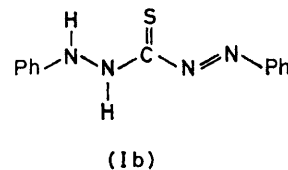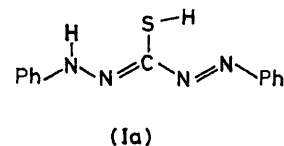
EXPERIMENTAL

Oscillation, Weissenberg, and precession photographs confirmed the previous choice of space group;[8] β^* was measured on the $h0l$ precession photograph.

Crystal Data.—$C_{13}H_{12}N_4S$, $M = 256$, monoclinic, $a = 4.70(1)$, $b = 22.25(3)$, $c = 11.95(2)$ Å, $\beta = 98.0(3)°$, $U = 1\ 238(3)$ Å^3, $D_m = 1.35$, $Z = 4$, $D_c = 1.37$ g cm^{-3}, $F(000) = 536$. Space group $P2_1/n$. Cu-K_α radiation, $\lambda = 1.541\ 8$ Å; μ(Cu-K_α) = 21.1 cm^{-1}.

(The angle β is given as 91.8° by Alsop;[8] the correct value, consistent with his indexing of the reflections, would be 82.0°.)

Multiple-film unintegrated intensity data were collected from a crystal of dimensions $0.9 \times 0.3 \times 0.1$ mm by the

[1] H. Fisher, *Angew. Chem.,* 1937, **50,** 919.
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[11] M. Harding, M. J. Adams, P. A. Alsop, and H. M. N. H. Irving, *Analyt. Chim. Acta,* 1973, **67,** 204.
[12] Y. Kushi and Q. Fernando, *Chem. Comm.,* 1969, 1240; *J. Amer. Chem. Soc.,* 1970, **92,** 1965.
[13] G. D. Andreetti, P. Domiano, G. F. Gasparri, M. Nardelli, and P. Sgarabotto, *Acta Cryst.,* 1970, **B26,** 1005.
[14] A. Kálmán, Gy. Argay, and M. Czugler, *Cryst. Struct. Comm.,* 1972, **1,** 375.
[15] M. Czugler, A. Kálmán, and Gy. Argay, *Cryst. Struct. Comm.,* 1973, **2,** 655.
[16] P. A. Alsop and H. M. N. H. Irving, *Analyt. Chim. Acta,* 1973, **65,** 202.
[17] A. C. Fabretti and G. Peyronel, *J. Inorg. Nuclear Chem.,* 1975, **37,** 603.

equi-inclination Weissenberg method with Ni-filtered Cu-K_α radiation for layers $0kl$ to $3kl$. The intensities were measured by the S.R.C. Microdensitometer Service (Rutherford Laboratory, Didcot England) and after merging and averaging duplicate measurements, 547 unique data were obtained. The crystal did not scatter strongly, with the result that only about half the accessible reflections were observable above background. The strongest and weakest data were checked by visual estimation with a time-calibrated intensity strip. The intensities of some additional strong low-angle reflections were estimated from $h0l$, $h1l$, and $h2l$ precession photographs. Only Lorentz-polarization corrections were applied to the data.

The atomic co-ordinates of Alsop [8] were used as the starting point of the refinement. A structure-factor calculation (R 0.24) and observed Fourier map confirmed the general correctness of his solution and the structure was then refined isotropically by block-diagonal least-squares to R 0.13. The individual layers of data (h 0—3) were then rescaled, yielding R 0.105. The ten hydrogen atoms attached to the phenyl rings were added (R 0.091). The scale factors for each layer of data were again adjusted,

TABLE 1

Fractional atomic co-ordinates and isotropic thermal parameters, with estimated standard deviations in parentheses

	x	y	z	$B/\text{Å}^2$
S	0.926 4(8)	1.088 0(2)	0.056 7(3)	*
N(1)	1.316 (2)	1.010 6(4)	0.200 0(7)	4.3(2)
N(2)	1.173 (2)	1.045 7(4)	0.258 8(7)	4.2(2)
N(3)	0.839 (2)	1.113 2(4)	0.272 5(7)	4.0(2)
N(4)	0.649 (2)	1.149 3(4)	0.220 2(7)	4.0(2)
C(1)	0.978 (2)	1.081 6(5)	0.200 9(8)	3.3(2)
C(2)	1.520 (2)	0.970 7(5)	0.250 0(8)	3.3(2)
C(3)	1.604 (3)	0.969 2(5)	0.368 0(9)	4.8(3)
C(4)	1.809 (3)	0.928 5(5)	0.413 9(10)	5.0(3)
C(5)	1.941 (3)	0.890 9(5)	0.344 6(10)	4.9(3)
C(6)	1.867 (3)	0.894 9(5)	0.231 0(9)	4.3(3)
C(7)	1.655 (2)	0.934 3(5)	0.181 9(9)	3.7(2)
C(8)	0.484 (2)	1.187 5(5)	0.277 2(9)	3.7(2)
C(9)	0.306 (3)	1.228 9(5)	0.213 3(9)	4.2(3)
C(10)	0.137 (3)	1.268 0(6)	0.265 7(11)	5.9(3)
C(11)	0.147 (3)	1.265 2(6)	0.380 8(10)	5.2(3)
C(12)	0.321 (3)	1.224 1(6)	0.442 7(11)	5.5(3)
C(13)	0.486 (3)	1.184 3(5)	0.389 6(10)	4.9(3)
H(3) †	1.510	1.000	0.419	
H(4)	1.858	0.927	0.498	
H(5)	2.095	0.862	0.381	
H(6)	1.973	0.866	0.181	
H(7)	1.607	0.939	0.097	
H(9)	0.308	1.230	0.129	
H(10)	0.011	1.296	0.218	
H(11)	0.014	1.293	0.420	
H(12)	0.344	1.225	0.528	
H(13)	0.596	1.151	0.436	
H(N1)	1.278	1.012	0.115	
H(N4)	0.618	1.149	0.134	

† All H atoms assigned B 5.0. * Anisotropic thermal parameters ($\times 10^4$) in the form: $\exp-[(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S	620(21)	30(1)	55(2)	53(10)	68(11)	1(3)

but thereafter were kept fixed. The sulphur atom was then assigned anisotropic parameters, and the parameters of the non-hydrogen atoms refined; R dropped to 0.080. A difference-Fourier map showed that the last two hydrogen atoms were attached to the nitrogen atoms N(1) and N(4).

* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1976, Index issue.

These hydrogen atoms were included in the structure factor calculations, and the parameters of the non-hydrogen atoms were then refined to convergence at R 0.068 for 547 observed data. A Hughes-type [18] weighting scheme was

FIGURE 1 A projection of the molecule on its mean plane, showing the numbering system and the more important bond lengths (Å)

used with 4 $F_{\text{min.}} = 20$. Scattering factors were for neutral atoms.[19] The F_c values of the unobserved reflections were satisfactorily small.

Final positional and thermal parameters are given in Table 1, while the numbering system is shown in Figure 1, and the mode of packing of the molecules in projection down a is illustrated in Figure 2.

FIGURE 2 A projection of the crystal structure down a, illustrating the mode of packing of the molecules. There are no short intermolecular contacts or hydrogen bonds

A map of the electron density in the mean plane of the molecule and the observed and calculated structure factors are given in Supplementary Publication No. SUP 22027 (6 pp., 1 microfiche).* Bond lengths and bond angles are listed in Table 2, intra- and inter-molecular non-bonded separations in Table 3, and the parameters for some least-squares planes in Table 4.

DISCUSSION

The results confirm the findings of Alsop [8] but show that the bond lengths and angles deduced by him are

[18] E. W. Hughes, *J. Amer. Chem. Soc.*, 1941, **63**, 1737.
[19] 'International Tables for X-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962, pp. 202, 204.

TABLE 2

Bond lengths (Å) and angles (°) *

(a) Distances

C(1)–S	1.71	C(5)–C(6)	1.36
C(1)–N(2)	1.34	C(6)–C(7)	1.40
C(1)–N(3)	1.35	C(7)–C(2)	1.36
N(1)–N(2)	1.30	C(8)–C(9)	1.39
N(3)–N(4)	1.29	C(9)–C(10)	1.39
C(2)–N(1)	1.38	C(10)–C(11)	1.37
C(8)–N(4)	1.39	C(11)–C(12)	1.37
C(2)–C(3)	1.41	C(12)–C(13)	1.38
C(3)–C(4)	1.38	C(13)–C(8)	1.35
C(4)–C(5)	1.38		

(b) Angles

S–C(1)–N(2)	124	N(2)–C(1)–N(3)	110
S–C(1)–N(3)	126	N(1)–C(2)–C(3)	122
C(1)–N(2)–N(1)	117	N(1)–C(2)–C(7)	119
C(1)–N(3)–N(4)	112	N(4)–C(8)–C(13)	122
N(2)–N(1)–C(2)	122	N(4)–C(8)–C(9)	118
N(3)–N(4)–C(8)	122		

Ring A: mean C–C–C 120°, C–C 1.38 Å.
Ring B: mean C–C–C 120°, C–C 1.37 Å.

* Probable errors: C–S, C–C, and C–N bonds in the chain 0.01 Å; C–C in Ph rings 0.02 Å; angles in N–N–C(S)–N–N system 1°.

TABLE 3

Inter- and intra-molecular distances (Å)

(a) Intramolecular non-bonded distances

N(1) ··· S	2.89	N(3) ··· C(13)	2.80
N(4) ··· S	2.84	N(2) ··· C(3)	2.82

(b) Intermolecular non-bonded separations

N(1) ··· N(3$^{\mathrm{I}}$)	3.38	C(7) ··· N(2$^{\mathrm{I}}$)	3.50
N(2) ··· N(4$^{\mathrm{I}}$)	3.30	C(8) ··· N(3$^{\mathrm{II}}$)	3.45
C(2) ··· N(2$^{\mathrm{I}}$)	3.48	C(9) ··· N(3$^{\mathrm{II}}$)	3.52
C(3) ··· N(2$^{\mathrm{I}}$)	3.56	C(10) ··· N(3$^{\mathrm{II}}$)	3.72
C(4) ··· N(2$^{\mathrm{I}}$)	3.74	C(11) ··· N(3$^{\mathrm{II}}$)	3.83
C(5) ··· N(2$^{\mathrm{I}}$)	3.79	C(12) ··· N(3$^{\mathrm{II}}$)	3.75
C(6) ··· N(2$^{\mathrm{I}}$)	3.65	C(13) ··· N(3$^{\mathrm{II}}$)	3.54

Roman numeral superscripts denote the following equivalent positions relative to the reference molecule at x, y, z:

$$\mathrm{I}\ x + 1, y, z;\quad \mathrm{II}\ x - 1, y, z.$$

TABLE 4

Equations of least-squares planes in the form $aX + bY + cZ = d$, where X, Y, and Z are orthogonal (Å) co-ordinates; deviations (Å) of atoms from the planes are given in square brackets

Plane (1): S, C(1), N(1)—(4)

$0.697X + 0.715Y + 0.049Z = 20.32$

[S 0.01, C(1) 0.00, N(1) −0.02, N(2) 0.03, N(3) 0.00, N(4) −0.01, C(2) −0.02, C(8) 0.02 Å]

Plane (2): C(2)—(7)

$0.717X + 0.695Y − 0.058Z = 19.68$

[C(2) 0.02, C(3) −0.02, C(4) 0.01, C(5) 0.01, C(6) −0.01, C(7) 0.00, N(1) 0.00, N(2) 0.05 Å]

Plane (3): C(8)—(13)

$0.738X + 0.664Y + 0.115Z = 19.25$

[C(8) 0.01, C(9) 0.00, C(10) 0.00, C(11) 0.00, C(12) 0.01, C(13) −0.01, N(4) 0.01, N(3) 0.14 Å]

incorrect because an incorrect value was used for the angle β. When 82° is used, reasonable agreement is obtained with the new molecular parameters. The molecule is near-planar, and closely approximates to

symmetry *mm* (see Figure 1) with the C–S bond lying on the intersection of the two mirror planes, but the phenyl rings twisted slightly out of the mean plane in opposite senses. Thus, C(3) and C(4) of ring A each lie 0.16 Å above the plane while it is C(9) and C(10) of ring B which are above the plane by 0.14 and 0.17 Å respectively.

In Table 5, bond lengths in dithizone are compared with those of related compounds. The pattern in the metal complexes consistently has the bond N(1)–N(2) shorter than N(3)–N(4), and C(1)–N(2) longer than C(1)–N(3) but the differences are small. In nearly all cases the N–C(Ph) distances are close to or shorter than 1.43 Å, implying that there is some delocalisation between the phenyl ring and the nitrogen system. The accuracy of the bond lengths in all the structures is not as high as the estimated standard deviations would imply, with the result that accurate bond orders cannot be deduced for the N–N and N–C bonds. Nevertheless, it is evident that the π electrons in the N–N–C–N–N chain are delocalised in all cases and that there are no localised single or double bonds. The sums of the estimated bond orders [20] for the nitrogen atoms in dithizone are: N(1) 3.85, N(2) 3.05, N(3) 3.05, and N(4) 3.85. As pointed out previously,[20] the *p* electrons on nitrogen in a conjugated carbon–nitrogen chain are delocalised if this atom is involved in three σ bonds (especially if one of these is to hydrogen). As a result, the sum of the bond orders of that nitrogen approaches 4. In the sydnone, dehydrodithizone,[12] the N–N bonds in the tetrazole system are ideally aromatic in character (1.313 and 1.318 Å) and the sum of the bond orders for the nitrogen atom bonded to the phenyl ring is 4.

Values for C–S bond lengths in the compounds related to dithizone range from 1.69 in dehydrodithizone[12] to 1.76 Å in S-methyldithizone,[9] and cluster around 1.73 Å in the primary metal dithizonates (see Table 5). It is possible to construct a curve relating the length of a S–C(sp^2) bond to its bond order. The reference compounds with the bond lengths [21-26] and bond orders are given in Table 6, and the relationship is shown graphically in Figure 3. As a test of the general correctness of the bond orders deduced for the C–S bonds (Table 5), one can assume that the sum of the bond orders for C(1) must always be 4, and then subtract from this the sum of the bond orders for C(1)–N(2) and C(1)–N(3) (see Figure 3 of ref. 20). The correspondence is satisfactory in all cases.

The bond lengths show that delocalisation in the N–N–C(S)–N–N system is a maximum in the sydnone,[12] intermediate in dithizone, and less in S-methyldithizone[9] which has a C–S bond order of 1.0. Diphenylthio-carbazide[11] formally has two N–N bonds of order 1, but the C–S and C–N bonds show that it too has electron delocalisation in the N–N–C–N–N chain.

[20] M. Burke-Laing and M. Laing, *Acta Cryst.*, 1976, **B32**, 3216.
[21] J. P. Chesick and J. Donohue, *Acta Cryst.*, 1971, **B27**, 1441.
[22] M. Fehlman, *Acta Cryst.*, 1970, **B26**, 1736.
[23] B. Krebs and D. F. Koenig, *Acta Cryst.*, 1969, **B25**, 1022.
[24] P. L. Johnson, E. C. Llaguno, and I. C. Paul, *J.C.S. Perkin II*, 1976, 234.
[25] A. Hordvik, *Acta Cryst.*, 1969, **A25**, S151.
[26] L. K. Hansen and A. Hordvik, *Acta Chem. Scand.*, 1970, **24**, 2246; 1973, **27**, 411.

TABLE 5

Comparison of bond lengths (Å) in dithizone with those in its complexes and related compounds [a]

Cpd.	C(1)–S	C(2)–N(1)	N(1)–N(2)	N(2)–C(1)	C(1)–N(3)	N(3)–N(4)	N(4)–C(8)
H₂dz	1.71	1.38	1.30	1.34	1.35	1.29	1.39
Ni(Hdz)₂ [b]	1.72(1)	1.43(2)	1.30(2)	1.35(2)	1.31(2)	1.33(2)	1.40(2)
Zn(Hdz)₂ [c]	1.76(01)	1.46(1)	1.28(01)	1.38(01)	1.32(01)	1.35(01)	1.44(1)
	1.76(01)	1.43(1)	1.27(01)	1.37(01)	1.31(01)	1.35(01)	1.41(1)
Zn(Hdz)₂ [d]	1.73(3)	1.40(4)	1.26(3)	1.30(3)	1.30(3)	1.32(3)	1.42(3)
	1.74(3)	1.43(4)	1.28(3)	1.40(3)	1.32(3)	1.34(3)	1.43(4)
Ni(Hdz)₂(bipy) [e]	1.71		1.33	1.37	1.36	1.33	1.48
	1.74		1.16	1.38	1.31	1.33	1.39
Hg(Hdz)₂(py)₂ [f]	1.64	1.42	1.25	1.41	1.36	1.25	1.44
SMe(Hdz) [g]	1.76(03)	1.42(05)	1.27(04)	1.39(04)	1.30(04)	1.34(04)	1.39(05)
H₄dz [h]	1.71	1.42	1.40	1.35	1.35	1.43	1.47

[a] The numbering system is that shown in Figure 1. An H atom is bonded to N(4) in all compounds, and N(1) is bonded to the metal in M(Hdz)₂. No standard deviations were quoted in ref. 11, ref. 6 gives ⩽0.04 Å, and in ref. 8 ca. 0.07 Å. Those of ref. 4 are internally inconsistent, some being ten times greater than others for bonds in similar environments. [b] Ref. 3. [c] Ref. 4. [d] Ref. 5. [e] Ref. 6. [f] Refs. 7 and 8. [g] Ref. 9. [h] Ref. 11.

The two hydrogen atoms of interest are bonded to N(1) and N(4). The coplanarity of both phenyl rings with the N–N–C–N–N chain confirms this observation

TABLE 6

Bond lengths (Å), with estimated standard deviations in parentheses and bond orders for C–S bonds where the C atom has sp^2 hybridisation

	Bond order		
	(a)	(b)	(c)
	1.0	1.5	2.0
Bond length	1.75	1.66	1.61

(a) S-Methyldithizone 1.76(03) [9]
  4,5-Dioxo-2-thioxo-1,3-dithiolan: 1.77, 1.74(06) [23]
  2-Mercaptobenzothiazole: 1.74, 1.73(04) [21]
  2-Methylaminobenzothiazole: 1.76, 1.74(03) [22]
(b) 3,4-Diphenylthiathiophthen: 1.65, 1.65(01) [24]
  2,3,4-Triphenylthiathiophthen: 1.67, 1.68(09) [25]
  Thiathiophthen: 1.67(09) [26]
(c) 4,5-Dioxo-2-thioxo-1,3-dithiolan: 1.61(06) [23]

because a hydrogen atom attached to either N(2) or N(3) would necessarily collide with H(3) or H(13) on rings A and B respectively and force the phenyl ring out
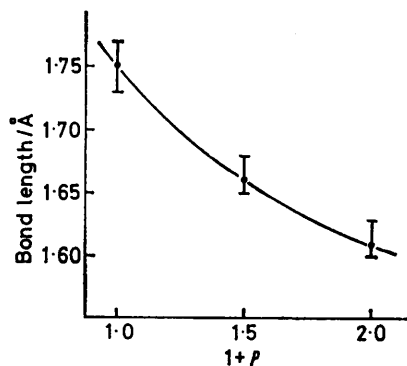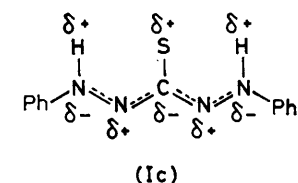

FIGURE 3 Relationship between bond order (1 + P) and reported bond lengths (Å) for S–C(sp²) bonds

of the plane of the molecule. Figure 2 shows that there are no close contacts of the type N · · · N or N · · · S between adjacent molecules, i.e. there are no inter-

[27] G. R. Form, E. S. Raper, and T. C. Downie, Acta Cryst., 1976, B32, 345.
[28] Yu. A. Omel'chenko, Yu. D. Kondrashev, S. L. Ginzburg, and M. G. Neigauz, J. Struct. Chem., 1973, 14, 533 (Zhur. strukt. Khim., 1973, 14, 574).

molecular hydrogen bonds parallel to b. (A hydrogen bond between S and N would have S · · · H · · · N ca. 3.35 Å.[13,21,27]) In 1,5-diphenylformazan,[28] and in

(Ic)

both forms of diazoaminobenzene,[29,30] the molecules are linked by strong hydrogen bonds (i.e. N · · · H · · · N between 3.22 and 3.26 Å). Since these compounds, as
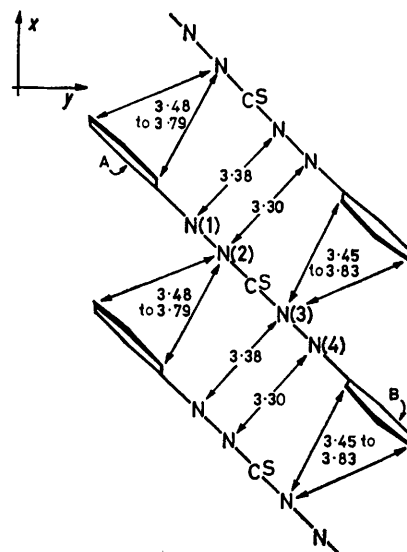

FIGURE 4 A projection of the structure down c showing three contacts

well as diphenylthiocarbazide,[11] are easily soluble in organic solvents, the extreme insolubility of dithizone cannot be due either to intermolecular hydrogen bonds or to the presence of the N–N–C(S)–N–N system.

[29] V. F. Gladkova and Yu. D. Kondrashev, Soviet Phys. Cryst., 1972, 17, 23 (Kristallografiya, 1972, 17, 33).
[30] V. F. Gladkova and Yu. D. Kondrashev, Soviet Phys. Cryst., 1972, 16, 806 (Kristallografiya, 1972, 16, 929).

Figure 4 is a projection of the structure down c showing the shortest intermolecular contacts; the closest are between nitrogen atoms on adjacent molecules stacked parallel to a. If the hydrogen atoms on N(1) and N(4) are assumed to carry a positive charge relative to these two nitrogen atoms, then it is possible to show that there is an alternation of positive and negative charge along the N-N-C-N-N chain, and the charge distribution and bonding in dithizone can be represented as in (Ic). This formulation is essentially identical with that deduced by Coleman and co-workers [31] from their n.m.r. and i.r. spectral studies.

Consideration of Figure 4 shows that the positively charged atom N(2) of the central molecule lies directly below and in contact with the negatively charged N(4) of the adjacent molecule, and above the π cloud of

hpenyl ring A of the molecule below. N(1) is attracted to N(3) of the molecule above. Thus, in any molecule, the four nitrogens are involved in four relatively strong electrostatic attractions to the nitrogen atoms in adjacent molecules while each of the two phenyl rings interacts with a nitrogen atom of one adjacent molecule. These strong attractive forces between the molecules stacked parallel to a cause the extreme insolubility of dithizone in organic solvents, and also account for the preferential growth of the crystal parallel to a, this being energetically the most-favoured direction.

[31] R. A. Coleman, W. H. Foster, J. Kazan, and M. Manson, *J. Org. Chem.*, 1970, **35**, 2039.