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The Crystal and Molecular Structures of 2,4-Diphenyl-2,3-benzodiazocin-1(2*H*)-one and 3a,8b-Dihydro-1,3-diphenylindeno[1,2-*c*]pyrazol-4(1*H*)-one

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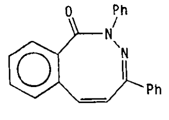
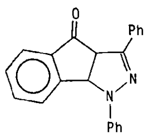
The molecular structures of 2,4-diphenyl-2,3-benzodiazocin-1(2*H*)-one, compound I, and 3a,8b-dihydro-1,3-diphenylindeno[1,2-*c*]pyrazol-4(1*H*)-one, compound II, have been determined by X-ray single-crystal diffraction methods. Compound II is a chemical isomer of compound I and is produced by thermal rearrangement of (I). Experimental details for compound I: triclinic, space group $P\bar{1}$, $Z=2$; $a=9{\cdot}753$ (2), $b=11{\cdot}116$ (4), $c=9{\cdot}202$ (2) Å, $\alpha=113{\cdot}12$ (2), $\beta=103{\cdot}23$ (2), $\gamma=102{\cdot}07$ (2)°, at −40°C; 2959 reflections [$I>2\sigma(I)$], ω-scans, Syntex diffractometer; full-matrix least-squares refinement of all atoms, $R=0{\cdot}039$. For compound II [where different from (I)]: monoclinic, space group $P2_1/c$, $Z=4$; $a=11{\cdot}017$ (3), $b=9{\cdot}386$ (2), $c=16{\cdot}222$ (2) Å, $\beta=107{\cdot}18$ (1)°, at −40°C; 1379 reflections; $R=0{\cdot}048$. Both molecules exist as discrete units. Compound I assumes the 'tub' conformation (no extensive π conjugation; crystals are colorless) with a very short C–H···O intramolecular distance, 2·23 Å. Compound II is found to have extensive π delocalization (crystals are greenish-yellow) within the Ph–C=N–N–Ph moiety.

Introduction

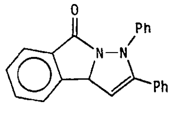
The crystal-structure determination of a synthesis product was undertaken in order to confirm the analysis of what was believed to be compound III (Katritzky, 1975). The actual structure was shown to be compound I, 2,4-diphenyl-2,3-benzodiazocin-1(2*H*)-one. Furthermore, during recrystallization of the material by sublimation at 140 °C, two crystalline forms were noted: long, colorless needles which were shown to be compound I and greenish-yellow prisms. It was thought that perhaps the greenish-yellow crystals were compound III, formed from (I) by ring-closure and a phenyl shift. However, a crystal-structure analysis revealed them to be compound II, 3a,8b-dihydro-1,3-diphenylindeno[1,2-*c*]pyrazol-4(1*H*)-one. The chemistry and preliminary structural information were communicated previously (Dennis, Katritzky, Lunt, Ramaiah, Harlow & Simonsen, 1976).



(I)



(II)



(III)

Experimental, structure solution and refinement

Crystals of compound I were supplied by A. R. Katritzky; crystals of compound II were grown by sublimation of (I) at a temperature of approximately 200 °C. At this higher temperature (higher than the 140 °C mentioned above), compound II is the sole product. Preliminary unit-cell parameters and space-group information were obtained from oscillation and Weissenberg photographs. All further work was carried out on a Syntex $P2_1$ diffractometer with the crystal

Table 1. *Experimental summary for compounds* I *and* II

	Compound I	Compound II
(*a*) Crystal data		
Formula	$C_{22}H_{16}N_2O$	$C_{22}H_{16}N_2O$
Formula weight	324·38	324·38
Crystal system	Triclinic	Monoclinic
Space group, Z	$P\bar{1}$, 2	$P2_1/c$, 4
Unit-cell parameters at −40 °C, Mo $K\alpha$ ($\lambda=0{\cdot}71069$ Å), refined by the least-squares method		
a	9·753 (2) Å	11·017 (3) Å
b	11·116 (4)	9·386 (2)
c	9·202 (2)	16·222 (2)
α	113·12 (2)°	
β	103·23 (2)	107·8 (1)°
γ	102·07 (2)	
V	841·8 Å^3	1602·7 Å^3
D_x	1·280 g cm^{-3}	1·344 g cm^{-3}
μ	0·86 cm^{-1}	0·90 cm^{-1}
Number of Bragg angles used in the refinement	43 ($23<2\theta<26°$)	38 ($11<2\theta<22°$)

Table 1 (*cont.*)

(*b*) Details of intensity measurements

Data collected at −40 °C on a Syntex $P2_1$ diffractometer		
Crystal dimensions	Ellipsoidal 0·21 × 0·31 mm	0·15 × 0·22 × 0·23 mm (001), (1$\bar{1}$0), (110)
Reflections measured	3853	2086
2θ range	4–55°	4–45°
Radiation	Mo $K\alpha$, graphite monochromator	
Mode	ω-scan technique (P counts accumulated)	
Scan range	±0·5° from $K\alpha$ peak	
Scan rate	Variable, 1·0–5·0° min^{-1} (defined as S)	
Background	Measured with ω set at ±1·0° from the $K\alpha$ peak, time of background measurements = scan time (B_1 and B_2 counts accumulated)	
Check reflections	Four reflections measured after every 96 reflections; only statistical variations noted	
I	$S(P-B_1-B_2)$	
$\sigma^2(I)$	$S^2(P+B_1+B_2)+(0{\cdot}02I)^2$	
Corrections made	Lorentz and polarization, no absorption	

(*c*) Details of structure refinements

Full-matrix least-squares refinement of all positional coordinates and thermal parameters (anisotropic for non-hydrogen atoms; isotropic for hydrogen atoms)		
Reflections refined, $I > 2\sigma(I)$	2959	1379
Variables	290	290
$R=\sum \lvert F_o\rvert - \lvert F_c\rvert /\sum\lvert F_o\rvert$	0·040	0·048
$R_w=[\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum w\lvert F_o\rvert^2]^{1/2}$	0·039	0·038
w	$1/\sigma^2(F_o)$	
Largest parameter shift in the final cycle	0·01σ	0·14σ
Largest peak in the final difference density map	0·16 e Å^{-3}	0·20 e Å^{-3}

cooled to −40 °C. Table 1 summarizes the experimental details with regard to crystal data, intensity measurements and structure refinements.

Both structures were solved by direct methods (*MULTAN*). In each case, the first cycles of full-matrix least-squares refinement were computed with all of the non-hydrogen atoms assigned the scattering factors of carbon. The nitrogen and oxygen atoms were then

Table 2. *Atomic coordinates for the non-hydrogen atoms of* 2,4-*diphenyl*-2,3-*benzodiazocin*-1(2*H*)-*one*, *compound* I, *with estimated standard deviations in parentheses*

	x	*y*	*z*
C(1)	0·2411 (2)	0·5341 (1)	0·1141 (2)
N(2)	0·2374 (1)	0·5175 (1)	0·2532 (1)
N(3)	0·1777 (1)	0·3784 (1)	0·2294 (1)
C(4)	0·2739 (1)	0·3153 (1)	0·2346 (2)
C(5)	0·4314 (2)	0·3713 (1)	0·2514 (2)
C(6)	0·4684 (2)	0·3885 (1)	0·1293 (2)
C(7)	0·3573 (1)	0·3579 (1)	−0·0307 (2)
C(8)	0·3669 (2)	0·2696 (2)	−0·1829 (2)
C(9)	0·2611 (2)	0·2322 (2)	−0·3348 (2)
C(10)	0·1449 (2)	0·2854 (2)	−0·3391 (2)
C(11)	0·1379 (2)	0·3786 (2)	−0·1913 (2)
C(12)	0·2421 (2)	0·4145 (1)	−0·0364 (2)
O(13)	0·2451 (1)	0·6423 (1)	0·1077 (1)
C(14)	0·2421 (2)	0·6233 (1)	0·4074 (2)
C(15)	0·3052 (2)	0·7633 (2)	0·4545 (2)
C(16)	0·3122 (2)	0·8624 (2)	0·6075 (2)
C(17)	0·2603 (2)	0·8261 (2)	0·7163 (2)
C(18)	0·1992 (2)	0·6879 (2)	0·6710 (2)
C(19)	0·1893 (2)	0·5862 (2)	0·5174 (2)
C(20)	0·2203 (1)	0·1734 (1)	0·2164 (2)
C(21)	0·0802 (2)	0·1209 (1)	0·2232 (2)
C(22)	0·0318 (2)	−0·0115 (2)	0·2057 (2)
C(23)	0·1202 (2)	−0·0941 (2)	0·1792 (2)
C(24)	0·2575 (2)	−0·0445 (2)	0·1705 (2)
C(25)	0·3083 (2)	0·0890 (2)	0·1896 (2)

Table 3. *Atomic coordinates for the non-hydrogen atoms of* 3a,8b-*dihydro*-1,3-*diphenylindeno*[1,2-*c*]-*pyrazol*-4(1*H*)-*one*, *compound* II, *with estimated standard deviations in parentheses*

	x	*y*	*z*
N(1)	0·2467 (3)	0·1889 (3)	0·4322 (2)
N(2)	0·2382 (3)	0·1019 (3)	0·4982 (2)
C(3)	0·1519 (3)	0·1515 (3)	0·5308 (2)
C(4)	0·0919 (4)	0·2866 (4)	0·4878 (2)
C(5)	0·1184 (3)	0·4137 (4)	0·5493 (2)
C(6)	0·2157 (3)	0·4998 (4)	0·5281 (2)
C(7)	0·2757 (4)	0·6213 (4)	0·5713 (3)
C(8)	0·3631 (4)	0·6894 (5)	0·5408 (3)
C(9)	0·3893 (4)	0·6384 (5)	0·4679 (3)
C(10)	0·3289 (4)	0·5178 (4)	0·4247 (3)
C(11)	0·2422 (3)	0·4490 (4)	0·4562 (2)
C(12)	0·1649 (3)	0·3157 (4)	0·4226 (2)
C(13)	0·3090 (3)	0·1418 (4)	0·3744 (2)
C(14)	0·2990 (4)	0·2162 (5)	0·2990 (2)
C(15)	0·3655 (4)	0·1697 (5)	0·2437 (3)
C(16)	0·4403 (4)	0·0517 (5)	0·2615 (3)
C(17)	0·4481 (4)	−0·0240 (5)	0·3359 (3)
C(18)	0·3837 (4)	0·0200 (4)	0·3925 (3)
C(19)	0·1188 (3)	0·0759 (4)	0·6002 (2)
C(20)	0·1939 (4)	−0·0342 (4)	0·6442 (2)
C(21)	0·1621 (5)	−0·1060 (5)	0·7086 (3)
C(22)	0·0531 (5)	−0·0696 (5)	0·7294 (3)
C(23)	−0·0212 (5)	0·0390 (5)	0·6874 (3)
C(24)	0·0095 (4)	0·1123 (4)	0·6221 (3)
O(25)	0·0664 (2)	0·4389 (3)	0·6040 (2)

easily singled out by the low value of their thermal parameters. The positions of the hydrogen atoms were later located in a difference-density Fourier map. The refined positional parameters for the non-hydrogen atoms are listed in Tables 2 and 3 for compounds I and II, respectively.* The computational details can be found elsewhere (Harlow, Loghry, Williams & Simonsen, 1974).

Discussion

The general conformation of the two molecules can be seen in Figs. 1 and 3, which also give the atom-numbering schemes (each hydrogen atom is numbered in accord with the carbon atom to which it is bonded). In both crystals the molecules exist as discrete units with no intermolecular contacts that are unusually short.

Compound I

Because of the conjugation within the amide group (including a resonance form of the type $^{-}O{-}C{=}N^{+}$) and the presence of the benzo moiety, it is not surprising that the eight-membered ring assumes the standard 'tub' conformation found for a number of analogous cyclooctatetraene compounds (Bordner, Parker & Stanford, 1972; and references therein). The tub is however quite distorted, not only in terms of the differing bond distances and angles (Fig. 2) associated with each of the functional groups which make up the ring, but also in its overall geometry as indicated by the irregularity of the torsion angles around the ring (Table 4) and the large deviations of the atoms from the planes calculated for the 'bottom' and 'top' of the tub (Table 5).

Of the four moieties which make up the eight-membered ring, the *N*-phenylamide group is the most interesting. This group, O=C–N–Ph, shows bond distances and angles which are very similar to those found for acetanilide (Brown, 1966). However, the dihedral angle between the amide and the phenyl planes in the present case is 24·1°, as opposed to approximately 38° for acetanilide. The smaller angle in the present case

Table 4. *Selected torsion angles for compound* I

Given a set of four atoms *A*, *B*, *C* and *D*, the torsion angle *ABCD* is defined as the angle between the two planes formed by *A*, *B*, *C* and *B*, *C*, *D*, respectively. When *A*, *B*, *C* and *D* are projected to a plane perpendicular to the line *BC*, along the direction from *B* to *C*, the sign of the torsion angle is defined as positive if the projected *D* is located within 180° clockwise rotation of *A* and negative otherwise.

C(1)—N(2)—N(3)—C(4)	87·2°	N(3)—C(4)—C(20)–C(25)	168·1°
C(1)—N(2)—C(14)–C(15)	−24·4	C(4)—N(3)—N(2)—C(14)	−111·7
C(1)—N(2)—C(14)–C(19)	158·8	C(4)—C(5)—C(6)—C(7)	1·9
C(1)—C(12)–C(7)—C(6)	14·2	C(5)—C(4)—C(20)–C(21)	171·1
C(1)—C(12)–C(7)—C(8)	−165·5	C(5)—C(4)—C(20)–C(25)	−9·8
C(1)—C(12)–C(11)–C(10)	169·9	C(5)—C(6)—C(7)—C(8)	−126·7
N(2)—C(1)—C(12)–C(7)	−61·9	C(5)—C(6)—C(7)—C(12)	53·6
N(2)—C(1)—C(12)–C(11)	130·0	C(6)—C(5)—C(4)—C(20)	109·1
N(2)—N(3)—C(4)—C(5)	−4·1	C(6)—C(7)—C(8)—C(9)	176·4
N(2)—N(3)—C(4)—C(20)	178·1	C(6)—C(7)—C(12)–C(11)	−178·2
N(3)—N(2)—C(1)—C(12)	−23·7	C(7)—C(12)–C(1)—O(13)	117·4
N(3)—N(2)—C(1)—O(13)	157·1	C(8)—C(7)—C(12)–C(11)	2·1
N(3)—N(2)—C(14)–C(15)	175·9	C(11)–C(12)–C(1)—O(13)	−50·7
N(3)—N(2)—C(14)–C(19)	−0·9	C(12)–C(1)—N(2)—C(14)	177·4
N(3)—C(4)—C(5)—C(6)	68·7	O(13)–C(1)—N(2)—C(14)	−1·9

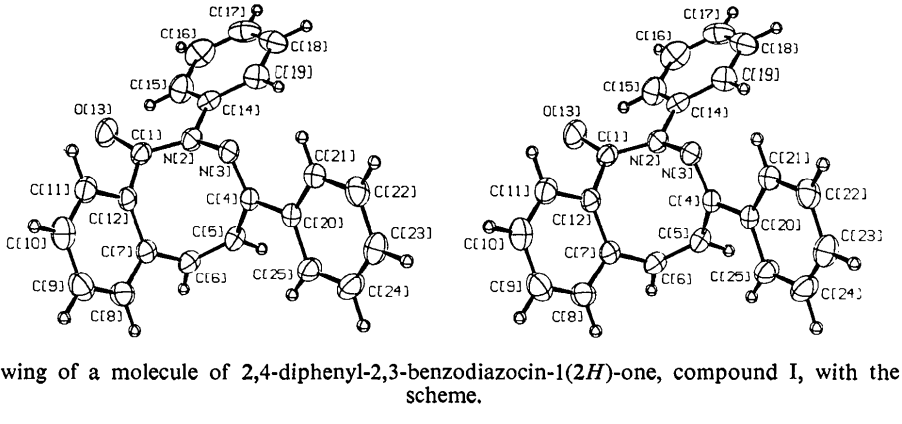


Fig. 1. Stereo drawing of a molecule of 2,4-diphenyl-2,3-benzodiazocin-1(2*H*)-one, compound I, with the atom-numbering scheme.

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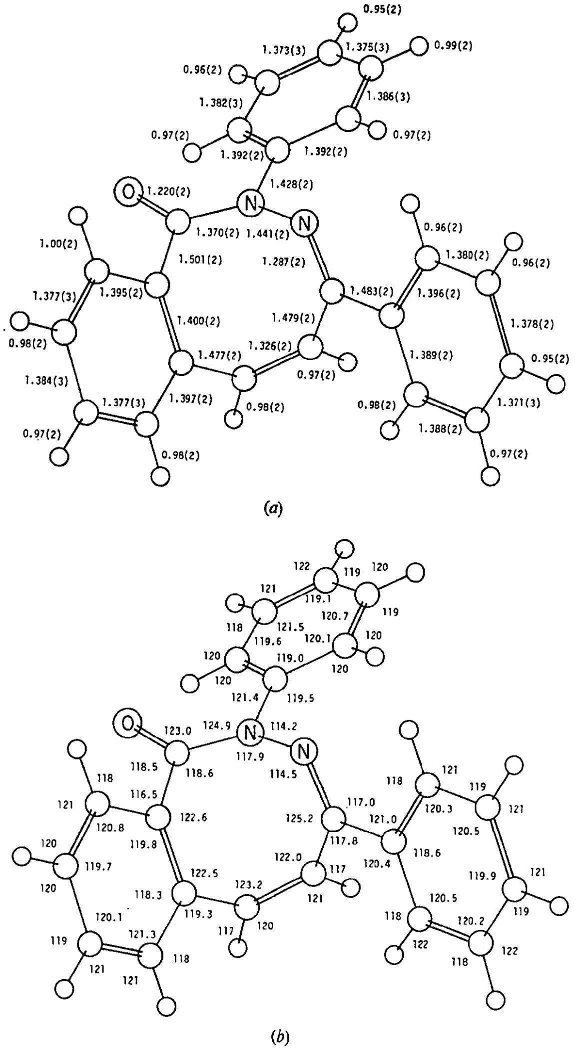
* Lists of structure factors, final positional parameters for the hydrogen atoms and thermal parameters for all atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31664 (33 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.



(a)

(b)

Fig. 2. (*a*) Bond distances and (*b*) angles for compound I. The average e.s.d. for angles involving non-hydrogen atoms is 0·2°; for angles involving a hydrogen atom, 1°.

places the *ortho*-hydrogen atom, H(15), only 2·23 Å away from the oxygen atom, O(13). Such very short C–H···O contacts (compared with 2·6 Å, the commonly-used sum of the van der Waals radii for hydrogen and oxygen) are becoming more and more prevalent (for example, Goldstein, 1975; Harlow, Simonsen, Pfluger & Sammes, 1974; and references therein). Whether such contacts can be classified as 'hydrogen

Table 5. *Deviations* (Å) *of atoms from various mean planes calculated for compound* I

The atoms included in the plane calculation are indicated with an asterisk.

(*a*) 'Bottom of tub' plane (as defined in Fig. 1)

C(1)*	0·039 (2)	C(6)*	−0·040 (2)	C(7)	0·834 (2)
N(2)*	−0·043 (1)	N(3)	1·082 (1)	C(12)	0·975 (2)
C(5)*	0·044 (2)	C(4)	1·060 (1)		

(*b*) 'Top of tub' plane

N(3)*	−0·028 (1)	C(12)*	0·026 (2)	C(5)	−0·896 (2)
C(4)*	0·027 (1)	C(1)	−1·004 (2)	C(6)	−0·901 (2)
C(7)*	−0·025 (2)	N(2)	−1·150 (2)		

(*c*) Plane of the benzo moiety

C(7)*	−0·020 (2)	C(11)*	0·018 (2)	C(5)	−1·002 (2)
C(8)*	0·020 (2)	C(12)*	0·002 (2)	C(6)	−0·078 (2)
C(9)*	0·000 (1)	C(1)	0·280 (2)	O(13)	1·270 (1)
C(10)*	−0·019 (2)	N(2)	−0·580 (1)		

(*d*) Plane of the amide group

C(1)*	0·004 (2)	C(12)*	−0·001 (2)	N(3)	0·501 (1)
N(2)*	−0·001 (1)	O(13)*	−0·001 (1)	C(14)	−0·052 (2)

(*e*) Plane of the phenyl group bonded to N(2)

C(14)*	0·003 (2)	C(18)*	−0·003 (2)	N(3)	−0·129 (1)
C(15)*	−0·006 (2)	C(19)*	0·001 (2)	O(13)	0·829 (1)
C(16)*	0·004 (2)	C(1)	0·346 (2)		
C(17)*	0·001 (2)	N(2)	−0·054 (1)		

(*f*) Plane of the phenyl group bonded to C(4)

C(20)*	−0·003 (1)	C(23)*	−0·002 (2)	N(3)	0·242 (1)
C(21)*	0·005 (1)	C(24)*	0·004 (2)	C(4)	0·008 (1)
C(22)*	−0·003 (2)	C(25)*	−0·002 (2)	C(5)	−0·204 (1)

Dihedral angle: *d*–*e*, 24·1°.

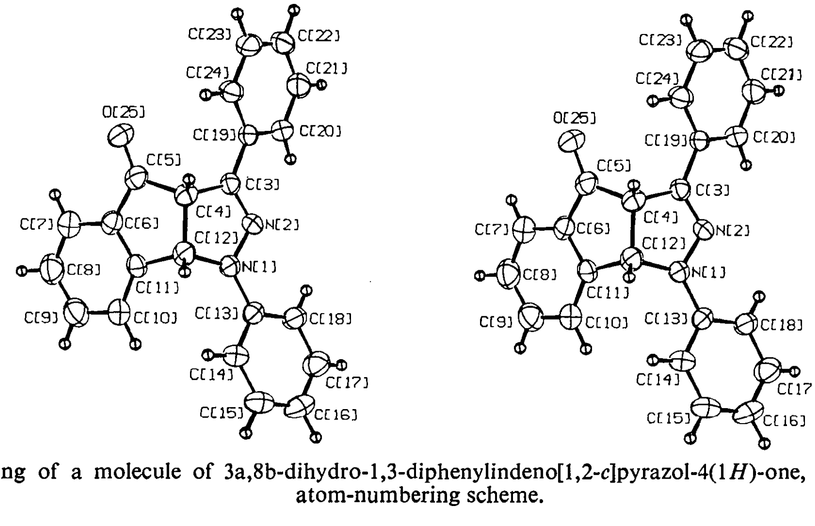


Fig. 3. Stereo drawing of a molecule of 3a,8b-dihydro-1,3-diphenylindeno[1,2-*c*]pyrazol-4(1*H*)-one, compound II, with the atom-numbering scheme.

bonds', or whether the van der Waals radii are in need of adjustment, awaits a definitive study.

The bond parameters associated with the phenyl–C=N– moiety are those expected for such a conjugated system: the N(3)–C(4)–C(20)–C(21) torsion angle is −11·0° and the C=N bond, 1·287 Å, shows a bond order somewhat less than two. On the other hand, the C=C moiety, with a bond distance of 1·326 (2) Å, exhibits pure double-bond character. The only unusual aspect of the benzo group arises from the mean-plane calculation for this group; although reasonably planar itself, the two atoms which are bonded to it, C(1) and C(6), deviate considerably from the plane, 0·280 (2) and −0·078 (2) Å, respectively.

Compound II

This molecule is characterized by two structural features. The first is the extended π systems of the benzo-C=O and the Ph-C=N-N-Ph moieties; the latter undoubtedly gives rise to the greenish-yellow color of the crystals. From the torsion angles (Table 6) and the calculated mean planes (Table 7), it is seen that the carbonyl group is only slightly out of the plane of the benzo moiety. The Ph-C=N-N-Ph moiety, while not perfectly planar throughout, has no torsion angles differing from 0 or 180° by more than 14°; both phenyl groups have dihedral angles slightly greater than 13° with respect to the plane of the five-membered heterocyclic ring. The overall conformation of the moiety is

Table 6. *Selected torsion angles for compound* II

N(1)—N(2)—C(3)—C(4)	−1·0°	C(4)—C(5)—C(6)—C(11)	6·1°
N(1)—N(2)—C(3)—C(19)	177·3	C(4)—C(12)–N(1)—C(13)	162·6
N(1)—C(12)–C(4)—C(3)	4·7	C(4)—C(12)–C(11)–C(6)	−3·2
N(1)—C(12)–C(4)—C(5)	122·9	C(4)—C(12)–C(11)–C(10)	176·7
N(1)—C(12)–C(11)–C(6)	−113·0	C(5)—C(4)—C(3)—C(19)	65·7
N(1)—C(12)–C(11)–C(10)	66·9	C(5)—C(4)—C(12)–C(11)	6·6
N(2)—N(1)—C(12)–C(4)	−5·8	C(5)—C(6)—C(7)—C(8)	−178·8
N(2)—N(1)—C(12)–C(11)	105·5	C(5)—C(6)—C(11)–C(10)	178·3
N(2)—N(1)—C(13)–C(14)	168·2	C(5)—C(6)—C(11)–C(12)	−1·9
N(2)—N(1)—C(13)–C(18)	−12·6	C(6)—C(5)—C(4)—C(12)	−7·8
N(2)—C(3)—C(4)—C(5)	−116·1	C(6)—C(11)–C(10)–C(9)	0·6
N(2)—C(3)—C(4)—C(12)	−2·6	C(7)—C(6)—C(5)—O(25)	5·8
N(2)—C(3)—C(19)–C(20)	12·5	C(7)—C(6)—C(11)–C(10)	−0·3
N(2)—C(3)—C(19)–C(24)	−166·4	C(7)—C(6)—C(11)–C(12)	179·6
C(3)—N(2)—N(1)—C(12)	4·5	C(9)—C(10)–C(11)–C(12)	−179·2
C(3)—N(2)—N(1)—C(13)	−164·8	C(11)–C(6)—C(5)—O(25)	−172·6
C(3)—C(4)—C(5)—C(6)	103·9	C(11)–C(12)–N(1)—C(13)	−86·1
C(3)—C(4)—C(5)—O(25)	−77·3	C(12)–N(1)—C(13)–C(14)	0·5
C(3)—C(4)—C(12)–C(11)	−111·7	C(12)–N(1)—C(13)–C(18)	179·7
C(4)—C(3)—C(19)–C(20)	−169·5	C(12)–C(4)—C(3)—C(19)	179·2
C(4)—C(3)—C(19)–C(24)	11·6	C(12)–C(4)—C(5)—O(25)	171·0
C(4)—C(5)—C(6)—C(7)	−175·5		

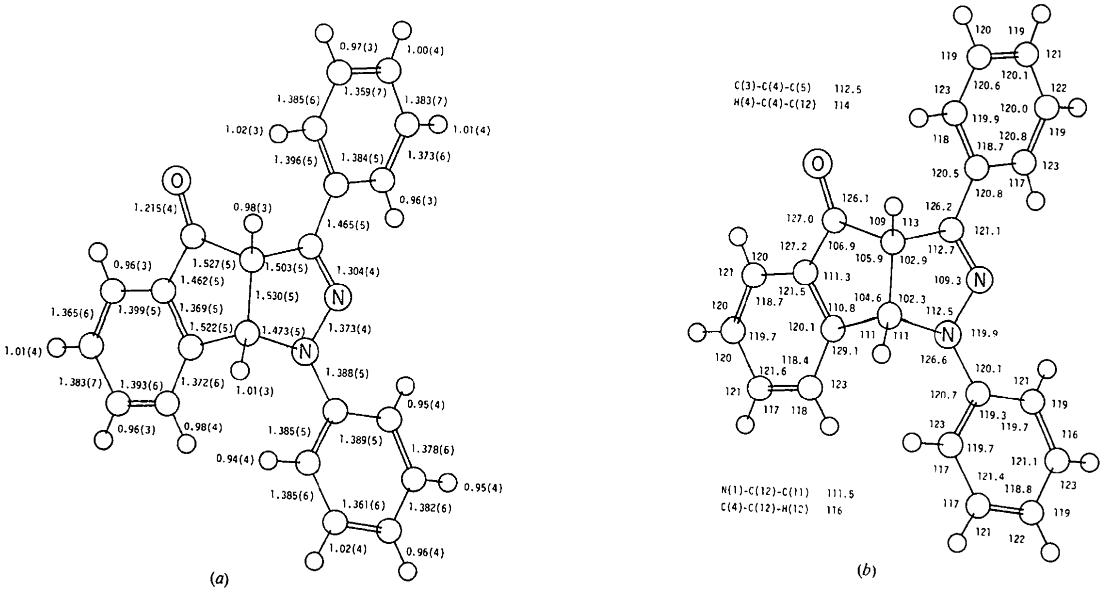


Fig. 4. (*a*) Bond distances and (*b*) angles for compound II. The average e.s.d. for angles involving non-hydrogen atoms is 0·4°; for angles involving a hydrogen atom, 2°.

perhaps best viewed in Fig. 3. The bond distances for C(13)–N(1), N(1)–N(2), N(2)–C(3), and C(3)–C(19) (Fig. 4) are all indicative of bond orders between one and two.

Table 7. *Deviations* (Å) *of atoms from various mean planes calculated for compound* II

The atoms included in the plane calculation are indicated with an asterisk.

(*a*) Plane of the five-membered ring containing two nitrogen and three carbon atoms

N(1)*	0·031 (3)	C(4)*	0·024 (4)	C(11)	−1·397 (4)
N(2)*	−0·015 (3)	C(12)*	−0·032 (4)	C(13)	0·349 (4)
C(3)*	−0·008 (3)	C(5)	−1·232 (4)	C(19)	0·008 (4)

(*b*) Plane of the five-membered ring, all carbon atoms

C(4)*	−0·046 (4)	C(12)*	0·032 (4)	C(8)	−0·104 (5)
C(5)*	0·043 (4)	N(1)	−1·213 (3)	C(9)	−0·079 (5)
C(6)*	−0·024 (4)	C(3)	−1·400 (3)	C(10)	−0·027 (4)
C(11)*	−0·006 (4)	C(7)	−0·068 (4)	O(25)	0·170 (3)

(*c*) Plane of the benzo moiety

C(6)*	−0·001 (4)	C(10)*	0·004 (4)	C(12)	−0·018 (4)
C(7)*	0·004 (4)	C(11)*	−0·003 (4)	O(25)	0·166 (3)
C(8)*	−0·004 (5)	C(4)	−0·106 (4)		
C(9)*	0·000 (5)	C(5)	0·031 (4)		

(*d*) Plane of the phenyl group bonded to N(1)

C(13)*	−0·008 (4)	C(16)*	−0·008 (5)	N(1)	−0·048 (3)
C(14)*	0·006 (4)	C(17)*	0·006 (4)	N(2)	0·182 (3)
C(15)*	0·002 (4)	C(18)*	0·002 (4)	C(12)	−0·069 (4)

(*e*) Plane of the phenyl group bonded to C(3)

C(19)*	0·000 (3)	C(22)*	0·006 (5)	N(2)	0·282 (3)
C(20)*	0·001 (4)	C(23)*	−0·005 (5)	C(3)	0·021 (3)
C(21)*	−0·004 (4)	C(24)*	0·002 (4)	C(4)	−0·199 (4)

Dihedral angles: *a–b*, 115·5; *a–d*, 13·3; *a–e*, 13·0; *b–c*, 2·0°.

The second feature is the nature of the two fused (*cis*) five-membered ring systems. Both rings are nearly planar (Table 7) but each has assumed a slight amount of 'envelope' conformation: for the heterocyclic ring, atom C(12) is the flap of the envelope; for the ring containing all carbon atoms, it is atom C(4). If the two rings are treated as planes, one finds that the dihedral angle between the two is 115·5°. However, the torsion angles for N(1)–C(12)–C(4)–C(5) and C(3)–C(4)–C(12)–C(11) are 122·9 and −111·7°, respectively, and, in conjunction with the torsion angles associated with each individual ring, more clearly indicate the geometry about the two bridgehead atoms.

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The Crystal and Molecular Structure of Rubidium Tetrathiocyanatobismuthate(III)

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The crystal structure of $Rb[Bi(SCN)_4]$ has been determined by inspection of Patterson two-dimensional ($h0l$) and ($hk0$) syntheses. Refinement was carried out by the full-matrix least-squares method, including anisotropic thermal parameters, to a final R of 0·076. The refinement was based on three-dimensional intensities of 648 reflexions obtained with Cu $K\alpha$ radiation and measured using a non-integrating Zeiss photometer. The space group is $P2_12_12$ with $a=11{\cdot}24$, $b=7{\cdot}65$, $c=6{\cdot}52$ Å and $Z=2$. Each Bi atom is surrounded by four S atoms which form a trigonal bipyramid with bismuth at the centre. The fifth corner is occupied by the lone pair of the central atom. There are two types of SCN groups and these are slightly bent [S(1)–C(1)–N(1) = 165·5° and S(2)–C(2)–N(2) = 173·7°]. The bismuth–sulphur distances are 2·70 for S(1) and 2·87 Å for S(2). The Bi–N(2) distance (2·74 Å) corresponds to the sum of the ionic Bi radius and the van der Waals N radius, which suggests a weak interaction.

Introduction

The crystal structure of rubidium tetrathiocyanatobismuthate(III) has been determined as part of the programme of study of the structures of complex compounds with cations of Group V. We were particularly interested in the coordination of bismuth, in the structure of the SCN group and in the stereochemical influence of the lone pair of the Bi atom. In addition, the problems of the crystal chemistry of complexes of bismuth(III) have not so far been thoroughly examined.