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The Crystal and Molecular Structure of Dicarbonylnitrosyltriphenylstibinecobalt(0)

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$Co(CO)_2(NO)Sb(C_6H_5)_3$ crystallizes in space group $P2_1/n$ with $a=15{\cdot}697$, $b=9{\cdot}406$, $c=13{\cdot}624$ Å, $\beta=90{\cdot}04°$, $Z=4$. The structure has been determined by Patterson and Fourier methods and refined to an R value of 0·037, with three-dimensional diffractometer data. The structure consists of discrete monomeric units. The Co and Sb atoms display distorted tetrahedral geometries. Although the carbonyl and nitrosyl groups are not distinguishable on the basis of the R values, an ordered model seems to be the most reasonable in view of the values of the bond distances and angles around cobalt.

Most transition-metal nitrosyls contain nearly linear M–N–O bonds and, because of their similarity to carbonyl complexes, have been formulated as NO^+ complexes. On the other hand several transition-metal nitrosyls have M–N–O bonds close to 120° and have been formulated as NO^- complexes. The existence of these two classes of metal nitrosyls is well established for five- and six-coordinate complexes.

Less is known about four-coordinate metal nitrosyls. The M–N–O bond angle is close to linearity for the complexes $(Ph)_2PC{:}C(Ph)_2.(CF_2)_2.CF_2.Fe(NO)_2$ (177·4°: Harrison & Trotter, 1971), $Co(NO)(CO)(PPh_3)_2$ (177·4°: Albano, Bellon & Ciani, 1972), $Co(NO)(CO)_2PPh_3$ (178·5°: Ward, Caughlan, Voecks & Jennings, 1972; Albano, Bellon & Ciani, 1972) and $Co(NO)(CO)_2AsPh_3$ (177·0°: Gilli, Sacerdoti & Reichenbach, 1973). A remarkable deviation from linearity has been observed in $[Ir(NO)_2(PPh_3)_2]^+$ (163·5°: Mingos & Ibers, 1970), $Ni(N_3)(NO)(PPh_3)_2$ (152·7°: Enemark, 1971), $[Co(NO)_2I]_n$ (171°) and $[Fe(NO)_2I]_2$ (161°: Dahl, De Gil & Feltham, 1969). In spite of the different values of the M–N–O bond angles, all the M–N bond distances of these compounds fall in the range 1·61–1·77 Å, that is in the accepted range of bond lengths (Connelly, 1972) of the NO^+ transition-metal nitrosyls. Possible reasons for the deviation of the M–N–O bond angle from 180° have been discussed by Kettle (1965) and Enemark (1971) in terms of different interactions of the two π^* orbitals of each ligand with the metal d orbitals.

Of the possible compounds of the general formula $Co(NO)(CO)_2X$, the compounds with $X=CO$, PPh_3 and $AsPh_3$ have been studied. $Co(NO)(CO)_3$ was studied by g.e.d. (Brockway & Anderson, 1937) and was 'assumed' to have linear nitrosyl groups. The compounds with $X=PPh_3$ and $AsPh_3$ have M–N–O bond angles very close to 180° (see above), but the carbonyl and nitrosyl groups are indistinguishable because of disorder. The possibility that the compound with $X=SbPh_3$ might not show this kind of disorder led us to undertake the present crystallographic analysis.

Experimental

The compound was prepared by reaction of $Co(NO)(CO)_3$ and $Sb(C_6H_5)_3$ in tetrahydrofuran at 40°C in an atmosphere of argon. The crystals, recrystallized from acetone/methanol solutions, were stable for a long period.

Weissenberg and precession photographs indicated a monoclinic unit cell. Precise cell parameters were determined by least-squares refinement of the X-ray powder diffraction pattern, determined on a G.E. XRD-5 powder diffractometer with Co $K\alpha$ radiation. Crystal data are reported in Table 1.

Table 1. *Crystallographic data*

Dicarbonylnitrosyltriphenylstibinecobalt(0)

$C_{20}H_{15}CoNO_3Sb$	F.W. 498·03
Monoclinic	Space group $P2_1/n$
$a=15{\cdot}697$ (4) Å	$Z=4$
$b=\ 9{\cdot}416$ (3)	$F(000)=976$
$c=13{\cdot}624$ (3)	$D_{calc}=1{\cdot}64$ g cm^{-3}
$\beta=90{\cdot}04$ (2)°	$D_{meas}=1{\cdot}65$ g cm^{-3}
$V=2013{\cdot}6$ Å^3	

A suitable crystal with dimensions $0{\cdot}15\times0{\cdot}31\times0{\cdot}42$ mm was mounted along the b axis. The intensities were collected on an automatic Siemens four-circle diffractometer, using Zr-filtered Mo $K\alpha$ radiation and the $\omega/2\theta$ scan technique. All the independent reflexions with $\theta\le29°$ were collected. Out of the 5372 reflexions, 1840 were unobserved, a reflexion being considered as unobserved when $I_o \le 2\sigma(I_o)$.* The intensities were not corrected for absorption [μ(Mo $K\alpha$)=22·3 cm^{-1}; μR=0·33]. Lorentz and polarization corrections were made as usual. The scattering factors for the hydrogen atoms were taken from the data of Stewart, Davidson & Simpson (1965) and for all the other atoms from the data of Cromer & Waber (1965). Allowance was made for the $\Delta f'$ and $\Delta f''$ terms of the Co and Sb atoms (Cromer, 1965). The calculations were carried out on a CDC-6600 computer with the X-RAY 71 system of crystallographic programs.

Structure determination and refinement

The positions of the Co and Sb atoms were determined from the three-dimensional Patterson synthesis and used as a starting point for the Fourier synthesis. The positions of all the remaining non-hydrogen atoms were determined from this Fourier map.

In the subsequent refinement the N and C atoms in the nitrosyl and carbonyl groups were considered as composite 'CN atoms', having a scattering factor $\frac{1}{3}f_N+\frac{2}{3}f_C$. Three cycles of full-matrix least-squares refinement, varying the scale factor and the positional and isotropic thermal parameters for all the non-hydrogen atoms, reduced R to 0·090. The positions of the H atoms were calculated assuming a C–H bond length of 1·08 Å. Three full-matrix least-squares cycles, refining the non-hydrogen atoms anisotropically and the hydrogen atoms isotropically, reduced R [$=\sum(|F_o|-|F_c|)/\sum|F_o|$] to 0·037 and R_w [$=\sum w(|F_o|-|F_c|)/\sum w|F_o|$] to 0·044. The unobserved reflexions were not used during the refinement and only four of them were calculated as greater than the threshold value. Weights for the last cycle were calculated as $w=1/(3{\cdot}51-0{\cdot}138|F_o|+0{\cdot}0022|F_o|^2)$. In this cycle the largest shift/error was 0·17.

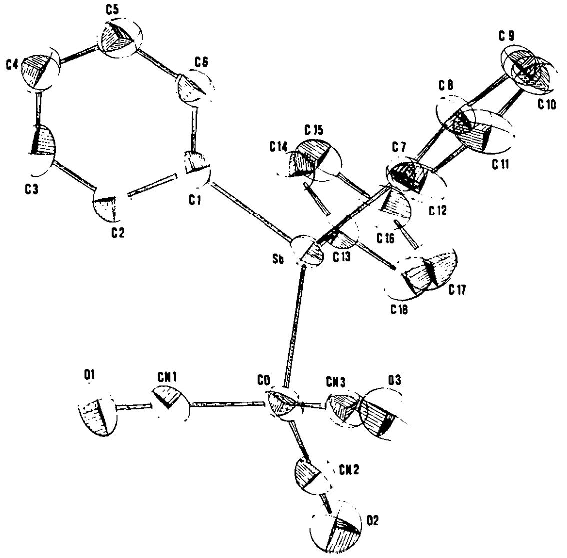

Fig. 1. Molecule of Co(NO) $(CO)_2Sb(C_6H_5)_3$, illustrating the thermal ellipsoids at 40% probability (Johnson, 1965).

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* The unobserved reflexions were assigned threshold values $I=I_0+2\sigma(I_0)$.

Table 2. *Positional* (× 10^4) *and thermal parameters of the non-hydrogen atoms*

Thermal parameters (Å^2) have been multiplied by 10^2. E.s.d.'s are shown in parentheses. The anisotropic temperature factor is of the form $\exp[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)]$.

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	664·6 (4)	2324·7 (8)	887·5 (5)	5·92 (4)	6·68 (4)	5·58 (4)	−0·29 (3)	0·73 (3)	2·02 (3)
Sb	322·6 (2)	1315·7 (3)	2521·5 (2)	4·47 (1)	3·71 (1)	4·71 (1)	0·17 (1)	0·53 (1)	0·74 (1)
CN(1)	1464 (3)	3585 (5)	1149 (4)	5·2 (2)	6·1 (3)	7·0 (3)	0·2 (2)	1·4 (2)	1·0 (2)
CN(2)	968 (3)	993 (5)	124 (4)	5·4 (2)	5·6 (3)	6·7 (3)	0·6 (2)	0·4 (2)	0·6 (2)
CN(3)	−274 (3)	3203 (6)	551 (4)	6·5 (3)	6·4 (3)	6·1 (3)	0·3 (2)	0·4 (2)	1·3 (2)
O(1)	1970 (3)	4409 (5)	1280 (4)	6·6 (2)	8·0 (3)	13·0 (4)	−2·0 (2)	1·3 (2)	−0·6 (3)
O(2)	1168 (3)	143 (5)	−437 (4)	9·1 (3)	9·1 (3)	11·5 (4)	2·1 (3)	0·0 (3)	−2·5 (3)
O(3)	−874 (3)	3787 (6)	313 (4)	7·7 (3)	12·4 (4)	11·2 (4)	3·3 (3)	−0·1 (3)	3·6 (3)
C(1)	977 (3)	2289 (4)	3706 (3)	5·6 (2)	3·4 (2)	5·6 (2)	0·0 (2)	0·0 (2)	0·6 (2)
C(2)	1859 (3)	2469 (6)	3629 (5)	5·5 (3)	5·3 (3)	8·1 (4)	0·7 (2)	−0·1 (2)	−0·4 (3)
C(3)	2306 (5)	3120 (7)	4365 (6)	6·4 (4)	7·6 (4)	10·0 (5)	−0·6 (3)	−2·2 (3)	−0·1 (3)
C(4)	1892 (5)	3617 (8)	5188 (5)	9·7 (5)	8·6 (4)	7·8 (4)	−2·1 (4)	−1·6 (4)	−0·8 (4)
C(5)	1014 (5)	3450 (7)	5275 (5)	10·2 (5)	8·2 (4)	6·8 (4)	−1·7 (4)	0·9 (3)	−1·3 (3)
C(6)	570 (4)	2789 (6)	4531 (4)	6·8 (3)	6·8 (3)	6·4 (3)	−1·3 (3)	1·2 (3)	0·1 (3)
C(7)	−964 (3)	1405 (5)	3024 (3)	4·8 (2)	6·0 (3)	4·9 (2)	0·5 (2)	0·3 (2)	0·1 (2)
C(8)	−1308 (3)	324 (6)	3569 (4)	5·5 (3)	5·1 (3)	6·9 (3)	−0·2 (2)	1·0 (2)	0·7 (2)
C(9)	−2154 (4)	379 (7)	3875 (5)	5·7 (3)	8·2 (4)	7·9 (4)	−0·9 (3)	2·0 (3)	0·1 (3)
C(10)	−2643 (4)	1514 (9)	3630 (5)	5·6 (3)	12·2 (6)	6·7 (3)	1·2 (4)	1·4 (3)	0·3 (4)
C(11)	−2302 (5)	2621 (9)	3111 (6)	8·0 (4)	12·3 (6)	9·5 (5)	5·3 (5)	2·5 (4)	2·9 (5)
C(12)	−1468 (4)	2565 (8)	2789 (5)	7·4 (4)	8·7 (4)	8·4 (4)	2·8 (3)	2·8 (3)	3·1 (3)
C(13)	608 (3)	−856 (5)	2804 (3)	5·0 (2)	3·8 (2)	5·5 (2)	0·6 (2)	0·7 (2)	0·3 (2)
C(14)	1046 (3)	−1272 (5)	3624 (4)	6·1 (3)	4·6 (2)	6·6 (3)	0·0 (2)	−0·2 (2)	0·7 (2)
C(15)	1237 (4)	−2682 (6)	3780 (5)	7·3 (4)	6·0 (3)	7·6 (4)	1·2 (3)	0·5 (3)	2·3 (3)
C(16)	988 (5)	−3682 (6)	3124 (5)	10·0 (4)	4·5 (3)	9·1 (4)	1·7 (3)	2·0 (3)	1·4 (3)
C(17)	535 (6)	−3305 (7)	2318 (6)	12·5 (6)	4·7 (3)	9·4 (5)	0·5 (3)	−0·3 (4)	−1·6 (3)
C(18)	353 (5)	−1877 (6)	2142 (6)	11·1 (5)	5·1 (3)	6·6 (3)	1·7 (3)	−1·2 (3)	−0·8 (3)

The final values of the positional and vibrational parameters are listed in the Tables 2 and 3.*

In addition to the disordered model, three ordered models corresponding to each of the possible positions of the N atom were refined. For the N atom substituting the CN(1), CN(2) and CN(3) atoms the R values are respectively:

N substituting CN(1):	$R=0{\cdot}038$	$R_w=0{\cdot}044$
N substituting CN(2):	0·037	0·044
N substituting CN(3):	0·038	0·045

These ordered refinements yielded atomic positions and bond distances and angles within 1σ of the corresponding values of the disordered refinement.

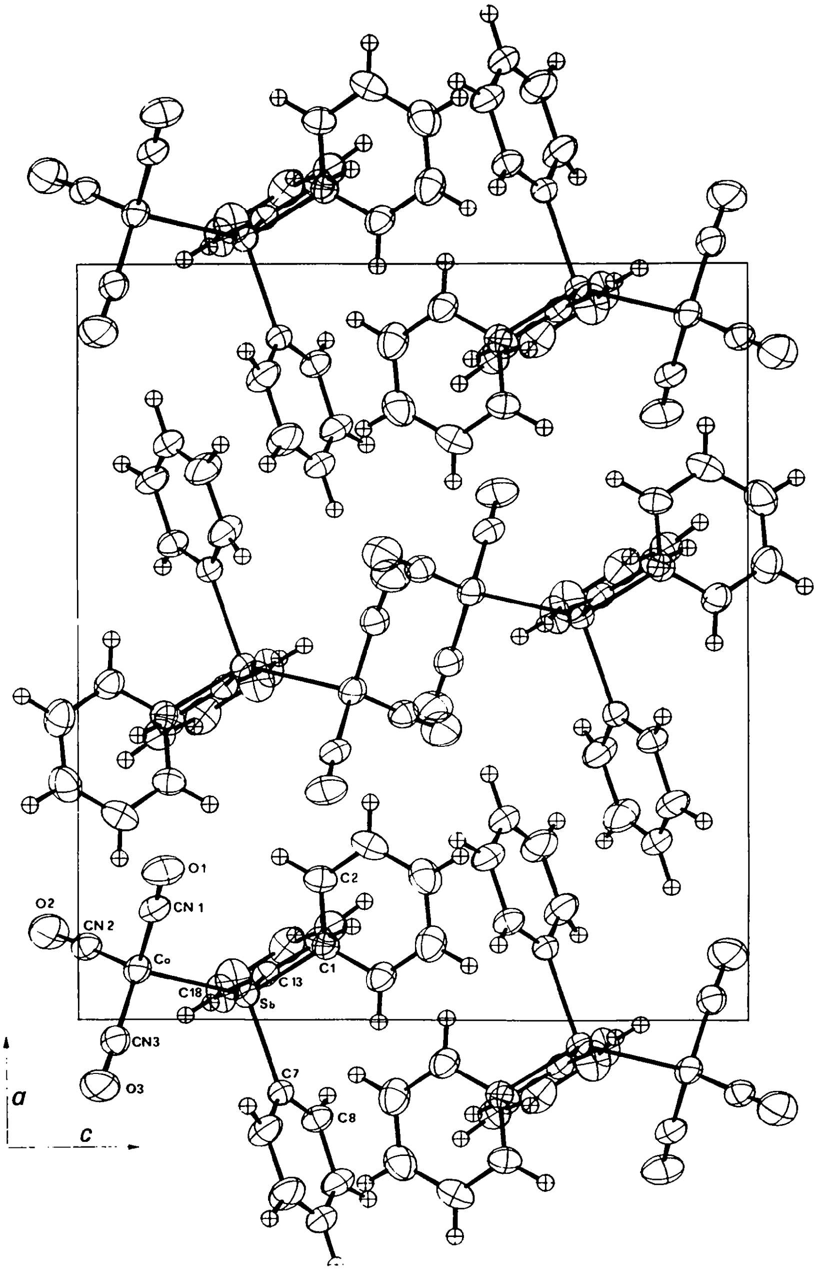

Fig. 2. Projection of the structure along **b** (Johnson, 1965).

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* A list of observed and calculated structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30372 (20 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Positional and thermal parameters of the hydrogen atoms*

Positional parameters are $\times 10^3$. Thermal parameters (Å^2) have been multiplied by 10^2. E.s.d.'s are in parentheses. The isotropic temperature factor is of the form $\exp(-8\pi^2 U \sin^2\theta/\lambda^2)$.

	x/a	*y/b*	*z/c*	*U*
H(2)	216 (4)	211 (8)	303 (5)	8·7 (20)
H(3)	286 (4)	320 (7)	438 (5)	7·8 (19)
H(4)	217 (5)	419 (8)	572 (6)	9·5 (22)
H(5)	73 (5)	392 (8)	584 (6)	11·2 (27)
H(6)	−3 (4)	276 (6)	450 (4)	6·0 (15)
H(8)	−100 (4)	−47 (6)	372 (4)	6·1 (15)
H(9)	−237 (5)	−37 (8)	433 (5)	9·9 (22)
H(10)	−324 (4)	161 (6)	385 (4)	6·5 (16)
H(11)	−263 (6)	335 (9)	285 (7)	12·2 (29)
H(12)	−113 (4)	343 (7)	253 (5)	8·0 (19)
H(14)	124 (3)	−61 (6)	410 (4)	6·4 (16)
H(15)	157 (4)	−291 (7)	428 (5)	7·7 (19)
H(16)	112 (4)	−477 (8)	325 (5)	9·0 (20)
H(17)	22 (6)	−400 (11)	198 (8)	15·4 (38)
H(18)	7 (5)	−154 (7)	161 (5)	8·8 (22)

Discussion

A projection of the structure along the *b* axis is shown in Fig. 1. The only intermolecular contacts are between carbonyl/nitrosyl oxygens and phenyl carbons. The intermolecular distances O(1)–C(14) = 3·18, O(2)–C(3) = 3·39 and O(2)–C(4) = 3·38 Å can be compared with the values of van der Waals radii of 1·77 for aromatic carbon and 1·50 Å for carbonyl oxygen (Bondi, 1964).

Table 4. *Bond distances* (Å)

E.s.d.'s are shown in parentheses.

Co—Sb	2·480 (1)	C(11)–C(12)	1·383 (10)
Co—CN(1)	1·763 (5)	C(12)–C(7)	1·385 (8)
Co—CN(2)	1·698 (5)	C(13)–C(14)	1·369 (7)
Co—CN(3)	1·750 (5)	C(14)–C(15)	1·378 (8)
O(1)—CN(1)	1·126 (7)	C(15)–C(16)	1·355 (9)
O(2)—CN(2)	1·150 (7)	C(16)–C(17)	1·355 (11)
O(3)—CN(3)	1·137 (8)	C(17)–C(18)	1·396 (9)
Co—O(1)	2·888 (5)	C(18)–C(13)	1·377 (8)
Co—O(2)	2·847 (5)	C(2)—H(2)	1·00 (7)
Co—O(3)	2·887 (5)	C(3)—H(3)	0·88 (7)
Sb—C(1)	2·121 (5)	C(4)—H(4)	0·99 (7)
Sb—C(7)	2·134 (4)	C(5)—H(5)	1·00 (8)
Sb—C(13)	2·129 (4)	C(6)—H(6)	0·94 (6)
C(1)—C(2)	1·399 (7)	C(8)—H(8)	0·91 (6)
C(2)—C(3)	1·368 (9)	C(9)—H(9)	1·00 (7)
C(3)—C(4)	1·378 (11)	C(10)–H(10)	0·99 (6)
C(4)—C(5)	1·392 (11)	C(11)–H(11)	0·93 (9)
C(5)—C(6)	1·379 (9)	C(12)–H(12)	1·03 (7)
C(6)—C(1)	1·376 (7)	C(14)–H(14)	0·95 (6)
C(7)—C(8)	1·371 (7)	C(15)–H(15)	0·89 (6)
C(8)—C(9)	1·393 (8)	C(16)–H(16)	1·06 (7)
C(9)—C(10)	1·357 (10)	C(17)–H(17)	0·94 (11)
C(10)–C(11)	1·367 (11)	C(18)–H(18)	0·91 (7)

Table 5. *Bond angles* (°)

E.s.d.'s are shown in parentheses.

Sb—Co—CN(1)	103·4 (2)	C(15)–C(16)–C(17)	120·2 (6)
Sb—Co—CN(2)	109·2 (2)	C(16)–C(17)–C(18)	120·0 (6)
Sb—Co—CN(3)	103·5 (2)	C(17)–C(18)–C(13)	120·0 (6)
CN(1)–Co—CN(2)	114·9 (2)	C(18)–C(13)–C(14)	118·7 (5)
CN(1)–Co—CN(3)	109·5 (2)	C(1)—C(2)—H(2)	119 (4)
CN(2)–Co—CN(3)	115·2 (2)	C(3)—C(2)—H(2)	121 (4)
Co—CN(1)–O(1)	177·3 (5)	C(2)—C(3)—H(3)	124 (4)
Co—CN(2)–O(2)	176·1 (5)	C(4)—C(3)—H(3)	115 (4)
Co—CN(3)–O(3)	178·3 (5)	C(3)—C(4)—H(4)	125 (4)
Co—Sb—C(1)	114·4 (1)	C(5)—C(4)—H(4)	115 (4)
Co—Sb—C(7)	118·6 (1)	C(4)—C(5)—H(5)	117 (5)
Co—Sb—C(13)	119·0 (1)	C(6)—C(5)—H(5)	123 (5)
C(1)—Sb—C(7)	101·3 (2)	C(5)—C(6)—H(6)	124 (3)
C(1)—Sb—C(13)	100·1 (2)	C(1)—C(6)—H(6)	114 (3)
C(7)—Sb—C(13)	100·3 (2)	C(7)—C(8)—H(8)	122 (3)
Sb—C(1)—C(2)	118·3 (4)	C(9)—C(8)—H(8)	118 (4)
Sb—C(1)—C(6)	123·0 (4)	C(8)—C(9)—H(9)	119 (4)
Sb—C(7)—C(8)	121·2 (4)	C(10)–C(9)—H(9)	121 (4)
Sb—C(7)—C(12)	119·8 (4)	C(9)—C(10)–H(10)	122 (3)
Sb—C(13)–C(14)	121·9 (4)	C(11)–C(10)–H(10)	118 (3)
Sb—C(13)–C(18)	119·4 (4)	C(10)–C(11)–H(11)	123 (6)
C(1)—C(2)—C(3)	120·4 (6)	C(12)–C(11)–H(11)	115 (6)
C(2)—C(3)—C(4)	120·4 (7)	C(11)–C(12)–H(12)	124 (4)
C(3)—C(4)—C(5)	119·9 (7)	C(7)—C(12)–H(12)	114 (4)
C(4)—C(5)—C(6)	119·3 (6)	C(13)–C(14)–H(14)	122 (4)
C(5)—C(6)—C(1)	121·3 (6)	C(15)–C(14)–H(14)	118 (4)
C(6)—C(1)—C(2)	118·7 (5)	C(14)–C(15)–H(15)	119 (4)
C(7)—C(8)—C(9)	120·7 (5)	C(16)–C(15)–H(15)	121 (4)
C(8)—C(9)—C(10)	119·6 (6)	C(15)–C(16)–H(16)	120 (4)
C(9)—C(10)–C(11)	120·4 (6)	C(17)–C(16)–H(16)	119 (4)
C(10)–C(11)–C(12)	120·3 (7)	C(16)–C(17)–H(17)	120 (7)
C(11)–C(12)–C(7)	119·8 (6)	C(18)–C(17)–H(17)	118 (7)
C(12)–C(7)—C(8)	119·1 (5)	C(17)–C(18)–H(18)	125 (4)
C(13)–C(14)–C(15)	120·7 (5)	C(13)–C(18)–H(18)	115 (4)
C(14)–C(15)–C(16)	120·4 (6)		

The shortest intermolecular distance between phenyl carbons is 3·66 Å for C(6)–C(15).

A drawing of the molecule, illustrating the thermal ellipsoids, is shown in Fig. 2. Bond distances and angles for the disordered model are reported in Tables 4 and 5.

The coordination around Sb is approximately tetrahedral. The mean Sb–C bond distance of 2·129 Å can be compared with the value of 2·13 Å found in $RhCl(SbPh_3)_2C_4(CF_3)_4 . CH_2Cl_2$ (Mague, 1970). A comparison of the molecular geometries of the phosphine, arsine and stibine groups is shown in Table 6. The mean value of the C–M–C angle decreases in the order P, As, Sb and is clearly correlated with the increase of the bond distance M–C and then of the intramolecular contact distance between the phenyl carbon atoms.

Table 6. *Comparison of bond lengths* (Å) *and angles* (°) *for the phosphine, arsine and stibine groups*

Study	M–Co	M–C	C–C	C–M–C
$Co(NO)(CO)_2P(C_6H_5)_3$[a]	2·224	1·820	2·85	103·2
$Co(NO)(CO)_2As(C_6H_5)_3$[b]	2·319	1·926	2·99	101·7
$Co(NO)(CO)_2Sb(C_6H_5)_3$[c]	2·480	2·129	3·27	100·6

(*a*) Ward, Caughlan, Voecks & Jennings (1972); Albano, Bellon & Ciani (1972).
(*b*) Gilli, Sacerdoti & Reichenbach (1973).
(*c*) Present study.

Maximum deviations from the least-squares planes of the three phenyl rings are 0·003, 0·013 and 0·013 Å for the rings containing respectively C(1), C(7) and C(13). The mean distance of the Sb atom from these planes is 0·044 Å. The phenyl rings are arranged in a helical way and are nearly mutually perpendicular. The C(1), C(7) and C(13) atoms are not symmetrically situated around the Co–Sb axis, as the two angles Co–Sb–C(7) and Co–Sb–C(13) are nearly equal (118·6 and 119·0°), but significantly different from the angle Co–Sb–C(1) of 114·4°.

The carbonyl-nitrosyl groups of the cobalt tetrahedron nearly eclipse the phenyl groups, the torsion angles C(1)–Sb–Co–CN(1), C(7)–Sb–Co–CN(3) and C(13)–Sb–Co–CN(2) being respectively 4·0, 9·3 and 8·5°.

The mean Co–CN and CN–O distances (1·74 and 1·14 Å) and the mean Co–CN–O angle (177·2°) are in agreement with the corresponding values found in the disordered phosphine and arsine derivatives, which are respectively 1·73, 1·14 Å and 178·8° for $Co(NO)(CO)_2PPh_3$ (Ward, Caughlan, Voecks & Jennings, 1972; Albano, Bellon & Ciani, 1972) and 1·74, 1·14 Å and 177·0° for $Co(NO)(CO)_2AsPh_3$ (Gilli, Sacerdoti & Reichenbach, 1973).

Because of the close linearity of the Co–CN–O bond angle the present compound could be formulated as a NO^+ complex, even though no additional information can be obtained from the infrared nitrosyl stretching frequency ($\nu_{NO} = 1762$ cm^{-1}), which is too close to the overlapping region for NO^+ and NO^- complexes (Connelly, 1972).

The general pattern of bond distances and angles around the Co atom shows that the groups CN(1)–O(1) and CN(3)–O(3) are symmetrically equivalent and different from the group CN(2)–O(2). This is apparent from an analysis of the bond angles around cobalt: CN(1)–Co–CN(2) ≃ CN(2)–Co–CN(3) ≃ 115·0°, CN(1)–Co–CN(3) = 109·5°; Sb–Co–CN(1) ≃ Sb–Co–CN(3) ≃ 103·4°, Sb–Co–CN(2) = 109·2°. The same symmetry can be observed from the bond and contact distances: Co–CN(1) ≃ Co–CN(3) ≃ 1·76 Å, Co–CN(2) = 1·70 Å; CN(1)–CN(2) ≃ CN(2)–CN(3) ≃ 2·91 Å, CN(1)–CN(3) = 2·87 Å.

Although we cannot distinguish between the different models solely on the basis of the R_w values, the ordered model with the N atom substituting CN(2) seems to be the most reasonable in view of the values of bond distances and angles.

As for the Co–CN bond distances, the difference between the observed values (1·76 and 1·70 Å) is in agreement with the difference between the M–C and M–N bond lengths found by Brockway & Anderson (1937) in $Co(CO)_3(NO)$ (Co–C = 1·83, Co–N = 1·76 Å) and in the isoelectronic compound $Fe(CO)_2(NO)_2$ (Fe–C = 1·84, Fe–N = 1·77 Å). The Co–C and Co–N bond distances in the present compound are considerably shorter than in $Co(CO)_3(NO)$. This shortening can be ascribed to the substitution of a carbonyl group by triphenylstibine. A similar effect has been observed in $Mn(CO)_4(NO)$ (containing linear Mn–N–O groups) with increasing substitution of the carbonyl groups by triphenylphosphine (Enemark & Ibers, 1967, 1968; Frenz, Enemark & Ibers, 1969); this effect has been interpreted as the result of the increased bond order of the remaining metal–carbon/nitrogen bonds, *via* π back-donation, caused by the smaller accepting ability of the substituting ligands.

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Structure Cristalline et Moléculaire du Benzotriazole

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Benzotriazole crystallizes in the space group $P2_1$ in a unit cell of dimensions $a=11\cdot92$, $b=23\cdot55$, $c=4\cdot13$ Å $\beta=94\cdot45°$. The unit cell contains 8 molecules. 2023 independent intensities were collected on an automatic diffractometer by a θ–2θ-scan method with Cu $K\alpha$ radiation. The structure was refined by full-matrix least-squares calculations to a conventional R of 0·056. The four independent molecules are planar and show the same configuration.

Dans le cadre d'une étude d'un ensemble d'hétérocycles azotés, il a été entrepris la détermination de la structure cristalline du benzotriazole $C_6N_3H_5$. La formule du benzotriazole pouvant s'écrire de deux façons différentes suivant la position de l'atome d'azote porteur de l'atome d'hydrogène [Fig. 1(*a*) et (*b*)] l'intérêt de ce travail était d'essayer de lever cette indétermination.

Partie expérimentale

Nous n'avons pu avoir de monocristaux convenables par les méthodes usuelles de cristallisation. Le cristal utilisé a été obtenu par fusion de zone sur un appareil construit au laboratoire. Il est cylindrique de diamètre 0,3 mm et a été taillé à 0,3 mm de longueur. Il a été monté de telle manière que l'axe *a* coïncide avec l'axe de la tête goniométrique.

Les études préliminaires ont été effectuées sur chambre de Weissenberg. Les paramètres ont été affinés par la méthode des moindres carrés à partir des mesures des angles de réflexions effectuées sur le diffractomètre qui a servi à la mesure des intensités. Les deux groupes $P2_1$ et $P2_1/m$ sont possibles d'après la loi d'extinction observée (extinction pour $0k0=2n+1$). La densité mesurée par la méthode de flottaison dans une solution d'IK indique la présence de huit molécules de benzotriazole par maille. Il y aura donc 4 ou 2 molécules cristallographiquement indépendantes par maille selon le groupe. Le test sur la distribution statistique des intensités normalisées n'a pas permis de déterminer d'une façon nette si le groupe était centré ou non. Nous avons choisi *a priori* le groupe $P2_1$, la suite du travail a confirmé la validité de cette hypothèse.

Les 2023 réflexions de sin $\theta/\lambda<0{,}6$ ont été mesurées sur un diffractomètre automatique Enraf Nonius, avec la radiation Cu $K\alpha$ et la méthode de balayage $\theta/2\theta$. Les intensités obtenues ont été corrigées du facteur Lorentz polarisation. Les effets d'absorption ont été

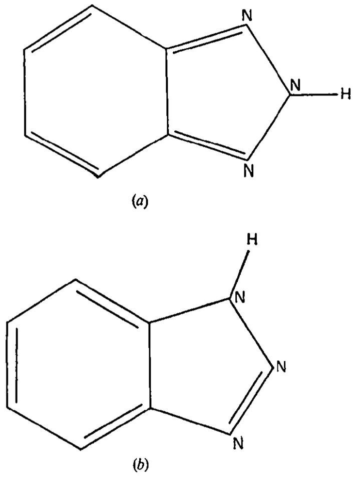

Fig. 1. Représentation des 2 types de molécules possibles.