

Table 2. Selected torsion angles

O(3)–C(2)–C(1)–O(1)	±164.5 (2)°
O(3)–C(2)–C(1)–O(2)	∓18.2 (4)
O(3)–C(2)–C(3)–C(4)	∓59.2 (4)
C(1)–C(2)–C(3)–C(4)	∓177.7 (3)
C(2)–C(3)–C(4)–C(5)	∓74.2 (3)
C(2)–C(3)–C(4)–N	±164.6 (3)

Table 3. Selected interatomic distances (Å) and angles (°)

Symmetry code				
(i)	$x,$	$y,$	$z$	(iv) $1-x, 2-y, -z$
(ii)	$1+x,$	$-1+y,$	$z$	(v) $1-x, 1-y, 1-z$
(iii)	$-x,$	$1-y,$	$1-z$	
$A-H \cdots B$	$A-H$	$H \cdots B$	$A \cdots B$	$\angle AHB$
O(1)–H(81) $\cdots$ Cl <sup>(iii)</sup>	0.99 (6)	2.03 (6)	3.019 (3)	175 (5)
O(3)–H(82) $\cdots$ Cl <sup>(iii)</sup>	0.89 (5)	2.33 (4)	3.126 (3)	149 (6)
N–H(71) $\cdots$ Cl <sup>(i)</sup>	0.98 (5)	2.27 (5)	3.242 (4)	172 (3)
N–H(72) $\cdots$ Cl <sup>(iv)</sup>	0.94 (4)	2.29 (5)	3.206 (3)	165 (5)
N–H(73) $\cdots$ O(3) <sup>(v)</sup>	0.95 (6)	2.14 (6)	3.028 (5)	154 (4)
N–H(73) $\cdots$ O(2) <sup>(v)</sup>	0.95 (6)	2.39 (5)	2.926 (4)	116 (3)

between the two cations related by a centre of symmetry at  $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ . Furthermore, there is a short contact between H(73) and the carbonyl O(2) (Table 3). Each Cl<sup>–</sup> ion is an acceptor for four hydrogen bonds from

four different molecules in the crystal. Thus, of the five available H atoms per cation, all are utilized in the formation of hydrogen bonds. All other intermolecular contacts correspond to van der Waals interactions.

This project was supported by the Danish Medical Research Council.

## References

- AHMED, F. R. (1968). NRC Crystallographic Program System, National Research Council, Ottawa, Canada.
- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
- HJEDS, H. & HONORÉ, T. (1978). *Acta Chem. Scand.* In the press.
- HONORÉ, T., HJEDS, H., KROGSGAARD-LARSEN, P. & CHRISTIANSEN, T. R. (1978). In preparation.
- International Tables for X-ray Crystallography* (1974). Vol. IV, p. 149. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1971). *ORTEP II*. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee.
- STEWART, E. G., PLAYER, R. B. & WARNER, D. (1973*a*). *Acta Cryst.* **B29**, 2038–2040.
- STEWART, E. G., PLAYER, R. B. & WARNER, D. (1973*b*). *Acta Cryst.* **B29**, 2825–2826.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
- TOMITA, K., HARADA, M. & FUJIWARA, T. (1973). *Bull. Chem. Soc. Jpn.* **46**, 2854–2858.
- TOMITA, K., HIGASHI, H. & FUJIWARA, T. (1973). *Bull. Chem. Soc. Jpn.* **46**, 2199–2204.
- XRAY system (1972). Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.

*Acta Cryst.* (1978). **B34**, 2361–2364

## Structure of the 1 : 1 Complex of Dimethyl Sulfoxide (DMSO) with 6-Hydroxy-1,3,7,9-tetranitroindazol[2,1-*a*]indazol-12-one

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(Received 25 July 1977; accepted 21 March 1978)

**Abstract.** C<sub>14</sub>H<sub>6</sub>N<sub>6</sub>O<sub>10</sub>·C<sub>2</sub>H<sub>6</sub>OS, monoclinic,  $P2_1/c$ ,  $a = 8.354$  (3),  $b = 11.750$  (5),  $c = 21.489$  (9) Å,  $\beta = 106.52$  (2)°,  $V = 2022$  Å<sup>3</sup>, four formula units per unit cell. There is a strong hydrogen bond between the hydroxyl H and the DMSO oxygen: H  $\cdots$  O 1.68, O  $\cdots$  O 2.57 Å,  $\angle O-H \cdots O$  166°.

**Introduction.** Workers in this laboratory have been engaged in a study of the photolysis of aqueous solutions of 2,4,6-trinitrotoluene ( $\alpha$ -TNT) (Burlinson, Kaplan & Adams, 1973; Kaplan, Burlinson & Sitzmann, 1975). The structure determination of the title complex was undertaken to identify a product obtained

Table 1. Atomic positions with *e.s.d.*'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>
C(1)	0.5752 (2)	-0.2365 (1)	0.45470 (7)	C(2)	0.6402 (2)	-0.2980 (1)	0.51109 (8)
C(3)	0.7707 (2)	-0.2498 (1)	0.55846 (7)	C(4)	0.8385 (2)	-0.1442 (1)	0.55244 (7)
C(5)	0.7647 (2)	-0.0862 (1)	0.49600 (7)	C(6)	0.8520 (2)	0.1215 (1)	0.51577 (7)
C(7)	0.7918 (2)	0.2122 (1)	0.46709 (7)	C(8)	0.8044 (2)	0.3311 (1)	0.46855 (8)
C(9)	0.7208 (2)	0.3970 (1)	0.41692 (9)	C(10)	0.6237 (2)	0.3418 (1)	0.36219 (8)
C(11)	0.6079 (2)	0.2255 (2)	0.35550 (8)	C(12)	0.6951 (2)	0.1621 (1)	0.40957 (7)
C(13)	0.5657 (2)	-0.0391 (1)	0.39587 (7)	C(14)	0.6340 (2)	-0.1299 (1)	0.44583 (7)
C(15)	0.0433 (5)	0.1776 (5)	0.1990 (1)	C(16)	-0.0813 (4)	0.0396 (4)	0.2712 (2)
H(1)	0.601 (2)	-0.374 (1)	0.5156 (7)	H(2)	0.922 (2)	-0.110 (1)	0.5872 (7)
H(3)	0.734 (2)	0.479 (1)	0.4171 (8)	H(4)	0.541 (2)	0.190 (1)	0.3166 (8)
H(5)	0.551 (2)	-0.060 (1)	0.3468 (8)	H(6)	0.357 (2)	0.029 (2)	0.3691 (8)
H(7)	0.151 (3)	0.218 (2)	0.192 (1)	H(8)	0.045 (4)	0.225 (3)	0.226 (1)
H(9)	-0.036 (3)	0.170 (2)	0.163 (1)	H(10)	-0.105 (3)	0.115 (2)	0.290 (1)
H(11)	-0.170 (3)	0.014 (2)	0.229 (1)	H(12)	-0.021 (3)	-0.038 (2)	0.291 (1)
N(1)	0.7069 (1)	0.0451 (1)	0.41447 (6)	N(2)	0.8008 (1)	0.0231 (1)	0.47927 (6)
N(3)	0.4370 (2)	-0.2874 (1)	0.40322 (8)	N(4)	0.8426 (2)	-0.3145 (1)	0.61814 (7)
N(5)	0.9205 (2)	0.3881 (1)	0.52434 (7)	N(6)	0.5349 (2)	0.4135 (1)	0.30605 (9)
O(1)	0.3944 (2)	-0.2410 (1)	0.35096 (7)	O(2)	0.3732 (2)	-0.3739 (1)	0.41639 (7)
O(3)	0.7521 (2)	-0.3822 (1)	0.63501 (6)	O(4)	0.9891 (1)	-0.2972 (1)	0.64743 (6)
O(5)	1.0508 (1)	0.3383 (1)	0.55108 (6)	O(6)	0.8819 (2)	0.4827 (1)	0.53939 (7)
O(7)	0.5483 (2)	0.5160 (1)	0.31161 (9)	O(8)	0.4526 (2)	0.3640 (1)	0.25772 (7)
O(9)	0.4217 (1)	0.0039 (1)	0.40793 (6)	O(10)	0.9271 (1)	0.12294 (9)	0.57290 (5)
O(11)	0.2343 (2)	0.1049 (1)	0.30751 (6)	S(1)	0.10890 (7)	0.05961 (7)	0.24784 (3)

in small quantities from the photolysis of an aqueous solution of 2,4-dinitroanthranil, itself a product of the photolysis of aqueous solutions of  $\alpha$ -TNT. The unknown material had been recrystallized from dimethyl sulfoxide, accounting for the 1:1 complex involving DMSO. From Weissenberg, oscillation and precession films, the systematic absences ( $h0l$ ,  $l = 2n + 1$ ;  $0k0$ ,  $k = 2n + 1$ ; space group  $P2_1/c$ ) and a preliminary set of cell dimensions were determined. A Picker four-circle diffractometer, with a Mo tube and graphite monochromator ( $\lambda = 0.71069 \text{ \AA}$ ), was used and  $2\theta$  measurements were made at both positive and negative positions for 17 reflections. These data were treated by a least-squares procedure\* yielding the cell dimensions given in the *Abstract*. Intensity data were collected using an  $\omega$ - $2\theta$  scan and an approximate hemisphere of reflections was measured to a  $2\theta$  maximum of  $55^\circ$ . Of the 7511 reflections so measured, 4872 were independent.

Intensity data were sorted and averaged with no corrections for absorption or extinction. Normalized structure factors were calculated using the program *NORMSF* and the structure was solved with the program *PHASE* using the intensity data to a  $2\theta$  maximum of  $37.5^\circ$ . The solution and refinement proceeded normally after the unanticipated DMSO molecule was identified. The refinement was accomplished using least-squares techniques, but because of the size of the problem, it was not possible to refine in

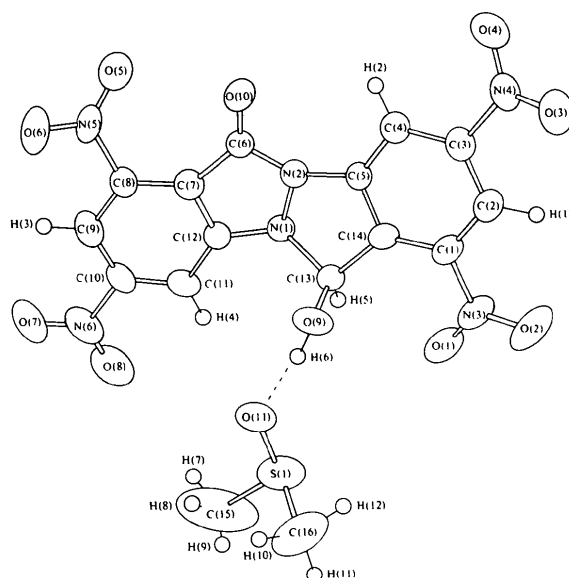


Fig. 1. ORTEP (Johnson, 1965) drawing of the complex.

the full-matrix mode. Rather, during each least-squares step, two matrices, two vectors, *etc.* were calculated, with approximately half the parameters in each block. The matrices were then treated separately with an overall scale factor included to relate the two blocks to each other. Further, to enhance the speed of the multi-cycle refinement steps, the two matrices were calculated on the first cycle only, with only structure factors and vectors calculated in subsequent cycles. In the final

\* All calculations, except those for thermal corrections to bond lengths, were performed on a CDC 6500 computer using either XRAY 72 (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) or XRAY 76 (Stewart, 1976).

refinement step, the matrices, vectors, *etc.* were calculated for each iteration. Of the 4638 non-systematically-absent reflections some 1644 had intensities less than  $2\sigma(I)$  and were classed too weak to have been measured reliably. In the least-squares cycles, these weak reflections were included only when the calculated structure factor  $F$  was greater than the observed  $F$ . With this scheme, using unit weights and anisotropic temperature factors for the nonhydrogen atoms and refining all parameters except  $U$  for H,\* the final  $R$  value is 0.054 (based on observed reflections only). The  $R$  value for all reflections is 0.089. The list of final positional parameters is given in Table 1, with the errors in the least significant place in parentheses.†

**Discussion.** An *ORTEP* drawing of the molecule showing the numbering system used in the parameter list is given in Fig. 1, and the bond lengths with errors in parentheses are given in Fig. 2. Fig. 3 shows the bond angles and errors for those bonds not involving H atoms, and Table 2 lists selected torsion angles.

This is the first structure to be reported containing the indazolo[2,1-*a*]indazole ring system, and while it bears certain formal similarities to indazole, there are differences between the structure of this molecule and that of indazole (Escande & Lapasset, 1974), even allowing for the presence of the C–N double bond in indazole that is absent here. Thus the N–C( $sp^2$ ) single bonds here are longer than in indazole [but shorter than would be predicted from single-bond radii (Camerman, 1970)] and C(6)–C(7) also is longer than the equivalent bond in indazole. The bond C(6)–N(2) is short compared to Camerman's predicted value of 1.470 Å for a C( $sp^2$ )–N( $sp^2$ ) single bond. Bond angles at

\* Temperature factors for the H atoms of the heterocyclic molecule were fixed at the values attained during the last isotropic refinement cycle for the atoms to which they are bonded. For the H atoms of the DMSO molecule,  $U$  values of 0.10 Å<sup>2</sup> were arbitrarily assigned.

† Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33478 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

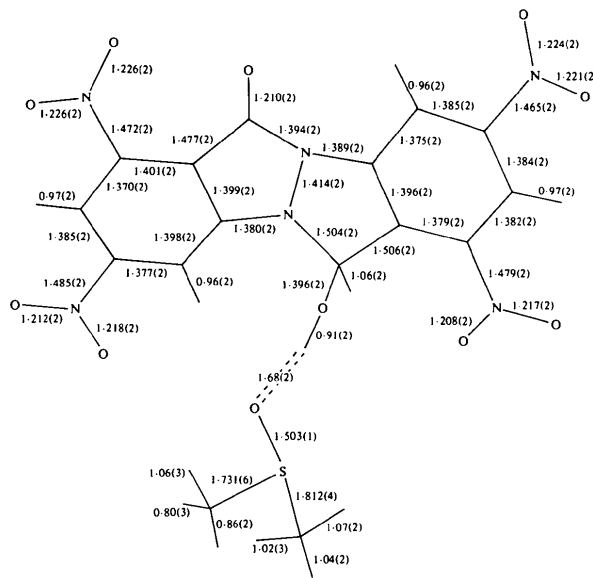


Fig. 2. Bond lengths (Å) with e.s.d.'s in parentheses.

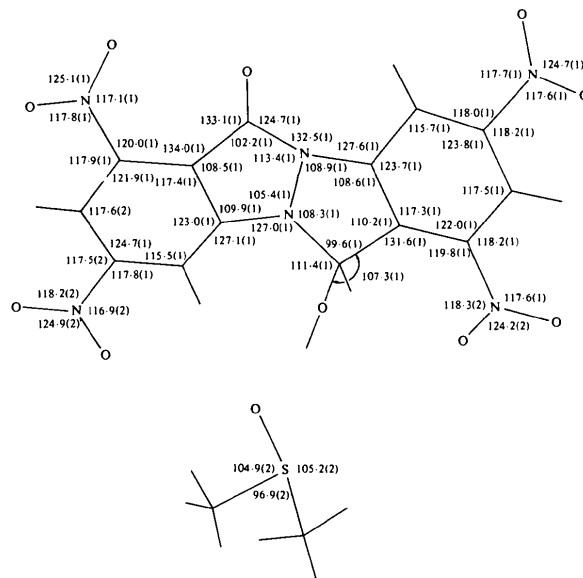


Fig. 3. Bond angles (°) with e.s.d.'s in parentheses.

Table 2. Selected torsion angles (°) with e.s.d.'s in parentheses

The sign convention is the 'right-hand rule' (Klyne & Prelog, 1960).

C(12)–C(7)–C(6)–O(10)	–173.2 (2)	C(12)–C(7)–C(6)–N(2)	7.0 (2)
C(7)–C(6)–N(2)–C(5)	–154.7 (2)	C(7)–C(6)–N(2)–N(1)	–3.7 (2)
C(6)–N(2)–N(1)–C(12)	–1.0 (2)	C(6)–N(2)–N(1)–C(13)	–139.5 (3)
N(2)–N(1)–C(12)–C(7)	5.7 (2)	N(2)–N(1)–C(13)–O(9)	92.2 (1)
N(2)–N(1)–C(13)–C(14)	–20.6 (3)	N(1)–C(12)–C(7)–C(6)	–8.1 (2)
N(1)–C(13)–C(14)–C(5)	16.6 (3)	C(13)–C(14)–C(5)–N(2)	–6.7 (2)
C(14)–C(5)–N(2)–N(1)	–7.2 (2)	C(14)–C(5)–N(2)–C(6)	144.8 (2)
C(5)–N(2)–C(6)–O(10)	25.5 (3)	C(5)–N(2)–N(1)–C(13)	18.4 (2)
C(5)–N(2)–N(1)–C(12)	156.8 (2)		

Table 3. *Thermal parameters for the DMSO molecule*

$$T = \exp[-2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{23}klb^*c^*)/100].$$

	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
S(1)	6.11 (3)	11.50 (5)	7.76 (4)	0.62 (3)	-0.02 (3)	-4.07 (4)
O(11)	5.62 (8)	8.1 (1)	6.28 (8)	0.85 (7)	-1.38 (6)	0.07 (7)
C(15)	11.4 (3)	31.9 (8)	5.6 (2)	4.0 (4)	-1.2 (2)	5.8 (3)
C(16)	7.8 (2)	15.4 (3)	13.9 (3)	-4.6 (2)	2.2 (2)	-6.9 (3)

chemically-equivalent atoms are in good agreement, with the exception of those with N as the apex atom. The angles at N(2) are all larger than those at N(1), but bond angles appear to be influenced strongly by relatively minor variations in chemical bonding (Domenicano, Vaciago & Coulson, 1975) which may also explain why the bond angles here differ from those in indazole. These differences in bond angles and the greater deviation of N(1) from the plane of its bonded atoms than the equivalent deviation for N(2), 0.36 vs 0.18 Å, are consistent with more  $sp^3$  character in the hybridization of N(1) than N(2). Bond lengths and angles in the remainder of the molecule are near commonly reported values. The nitro-group rotations\* are: at N(3) +10, at N(4) -27, at N(5) +36, and at N(6) -1°.

In the DMSO molecule, the bond lengths are similar to those reported for the crystal structure at 5°C of the free molecule (Thomas, Shoemaker & Eriks, 1966) in that one C-S bond is significantly shorter than the other. This difference in bond lengths disappears in the crystal structure at -60°C (Viswamitra & Kannan, 1966) where the C-S bond lengths agree with the longer value reported here and by Thomas, Shoemaker & Eriks. The value from a microwave determination of the DMSO structure (Feder, Dreizler, Rudolph & Typke, 1969) also supports this longer value. In view of the above and because the thermal parameters for the DMSO atoms are quite large in this structure (see Table 3), it is quite possible that the difference in bond lengths is due to thermal effects.† Corrections to the bond lengths for thermal motion (Busing & Levy, 1964) were calculated and the discrepancy between the two bond lengths was indeed reduced (from 0.081 to 0.049 Å by the 'riding-motion' correction, for example) but not eliminated. Bond angles C(15)-S(1)-O(11) and C(16)-S(1)-O(11) should be the same although

both angles are smaller than the values reported in the other works.

The two molecules of the solvate are joined by a very strong hydrogen bond, in agreement with the solution behavior of DMSO as a strong hydrogen-bond acceptor (Kamlet & Taft, 1976). The parameters of this hydrogen bond are similar to others reported for strong hydrogen bonds (Brown, 1976).

#### References

- BROWN, I. D. (1976). *Acta Cryst.* A32, 24-31.  
 BURLINSON, N. E., KAPLAN, L. A. & ADAMS, C. E. (1973). *Photochemistry of TNT*. Part I. Naval Ordnance Laboratory Tech. Rep. NOLTR 73-172.  
 BUSING, W. R. & LEVY, H. A. (1964). *Acta Cryst.* 17, 142-146.  
 CAMERMAN, A. (1970). *Can. J. Chem.* 48, 179-181.  
 DOMENICANO, A., VACIAGO, A. & COULSON, C. A. (1975). *Acta Cryst.* B31, 221-234.  
 ESCANDE, A. & LAPASSET, J. (1974). *Acta Cryst.* B30, 2009-2012.  
 FEDER, W., DREIZLER, H., RUDOLPH, H. D. & TYPKE, V. (1969). *Z. Naturforsch. Teil A*, 24, 266-278.  
 JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.  
 KAMLET, M. J. & TAFT, R. W. (1976). *J. Am. Chem. Soc.* 98, 377-383.  
 KAPLAN, L. A., BURLINSON, N. E. & SITZMANN, M. E. (1975). *Photochemistry of TNT*. Part II. Naval Surface Weapons Center Tech. Rep. NSWC/WOL TR 75-152.  
 KLYNE, W. & PRELOG, V. (1960). *Experientia*, 16, 521-523.  
 STEWART, J. M. (1976). The XRAY 76 system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.  
 STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1972). The XRAY system - version of June 1972. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.  
 THOMAS, R., SHOEMAKER, C. B. & ERIKS, K. (1966). *Acta Cryst.* 21, 12-20.  
 VISWAMITRA, M. A. & KANNAN, K. K. (1966). *Nature (London)*, 209, 1016-1017.

\* Rotation is positive if clockwise, when viewed from the center of the ring.

† Suggested by a referee.