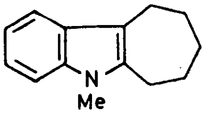
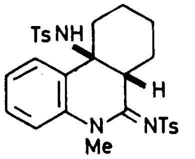
Crystal and Molecular Structure of *cis*-5,6,6a,7,8,9,10,10a-Octahydro-5-methyl-10a-*p*-tolylsulphonylamino-6-*p*-tolylsulphonyliminophenanthridine

By **Stephen R. Critchley, Keith Prout,*** and **David J. Watkin,** Chemical Crystallography Laboratory, 9 Parks Road, Oxford OX1 3PD
A. Sydney Bailey * and **Josephine M. Peach,** Dyson Perrins Laboratory, South Parks Road, Oxford OX1 3QY

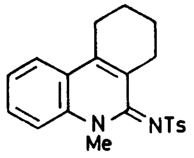
The structure of the title compound has been determined from *X*-ray data by direct methods. Crystals are monoclinic, $a = 12.509 \pm 0.007$, $b = 14.197 \pm 0.004$, $c = 15.666 \pm 0.009$ Å, $\beta = 102.10 \pm 0.03°$, space group $P2_1/n$. 3 099 Reflections were used and the structure refined by full-matrix least squares to R 0.043. The crystals are formed without intermolecular hydrogen bonding. Interatomic distances and interbond angles are unexceptional. The N–S bonds at the imino- (1.610 Å) and amino- (1.606 Å) nitrogen atoms are not significantly different. The molecular conformation is described.

REACTION of hexahydro-5-methylcyclohept[*b*]indole (1) with tosyl azide in pyridine solution gave a compound to which was ascribed formula (2). The compound did not eliminate toluene-*p*-sulphonamide ($TsNH_2$) when boiled with 1,5-diazabicyclo[4.3.0]non-5-ene; but it yielded (3) both on sublimation and on solution in trifluoroacetic acid. On boiling with alcoholic sodium hydroxide solution, (2) was hydrolysed to form (4) but did not eliminate $TsNH_2$. We therefore suggested [1,2] that the ring junction in compound (2) was *cis*. Compounds with similar properties have been obtained by the reaction of tosyl azide with compound (5) [3] and with compound (6).[4] Since no previous examples of compounds of this overall structure have been reported it was considered of importance that the stereochemistry of the ring junction in compound (2) should be established beyond doubt. Further, the *p*-tolylsulphonylamino-residue has a similar environment to that in (7).[5] In (7) the =N–S bond is unexpectedly short and the benzene ring of the indole residue is inert, indicating that the form (8) is an important contributor to the electronic structure.

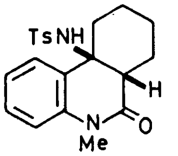

(1)



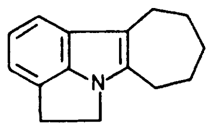
(2)



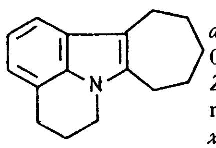
(3)



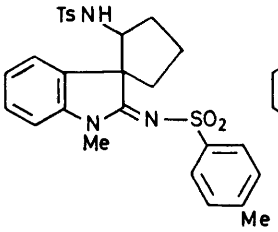
(4)



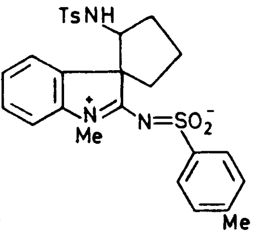
(5)



(6)



(7)



(8)

An *X*-ray structure analysis of (2) was carried out to establish the stereochemistry and to compare the dimensions of the sulphonylamino-residue with those in (7).

EXPERIMENTAL

The compound was recrystallised from chloroform–methanol.

Crystal Data.—$C_{28}H_{31}N_3O_4S_2$, $M = 537.7$, monoclinic, $a = 12.509 \pm 0.007$, $b = 14.197 \pm 0.004$, $c = 15.666 \pm 0.009$ Å, $\beta = 102.10 \pm 0.03°$, $U = 2\,720$ Å^3, $D_m = 1.303$, $Z = 4$, $D_c = 1.313$ g cm^{-3}. Space group $P2_1/n$ [C_{2h}^5, No. 14 non-standard setting, equivalent positions $\pm$ (x,y,z; $1/2 + x$, $1/2 - y$, $1/2 + z$)]; systematic absences: $h0l$, $h + l = 2n + 1$, $0k0$, $k = 2n + 1$. Mo-K_α radiation, $\lambda = 0.710\,7$ Å; μ(Mo-K_α) = 2.34 cm^{-1}.

Preliminary oscillation, Weissenberg, and precession photographs yielded approximate cell dimensions and indicated the crystal to be monoclinic, $P2_1/n$, b unique. A diamond-shaped crystal (0.6 × 0.7 × 0.4 mm) mounted about a was set up on a Hilger and Watts four-circle diffractometer and accurate cell dimensions and orientation matrix obtained by a least-squares best fit to the accurately determined setting angles of 32 reflections.[6] The intensities of at least two equivalents of each reflection for $\theta \leqslant 30°$ were collected by an ω—2θ scan with 60 steps of 0.02°, by use of ordinate analysis.[7] The 30 consecutive steps giving the highest total count were treated as peak and the remaining 30 as background. 3 099 unique reflections with $I > 3\sigma(I)$ remained after merging equivalents. Data were corrected for Lorentz and polarisation effects but not for absorption.

The structure was solved by weighted, multi-solution tangent refinement [8] on the phases of 506 reflections having $E > 1.3$. The origin was defined with the phases $\bar{6}$,1,1, 8,11,2, and $\bar{1}$,4,5. $\bar{3}$,7,3 and $\bar{3}$,1,2 were used as multi-solution phases. An E-map based on the phase set with

---

[1] A. S. Bailey and J. F. Seager, *J.C.S. Perkin I*, 1974, 763.

[2] A. S. Bailey and P. A. Wilkinson, *J.C.S. Perkin I*, 1976, 481.

[3] A. S. Bailey, P. A. Hill, and J. F. Seager, *J.C.S. Perkin I*, 1974, 967.

[4] P. A. Wilkinson, D.Phil Thesis, Oxford, 1975.

[5] I. J. Tickle and C. K. Prout, *J. Chem. Soc.* (*C*), 1971, 3401.

[6] M. Dobler and B. Duerr, personal communication.

[7] H. C. Watson, D. M. Shotten, J. M. Cole, and H. Muirhead, *Nature*, 1970, **225**, 806.

[8] G. Germain, P. Main, and M. M. Woolfson, *Acta Cryst.*, 1971, **A24**, 368.

the best figure-of-merit revealed all non-hydrogen atom positions in the structure. This model was refined by full-matrix least-squares with individual isotropic temperature factors and unit weights to R 0.140. The refinement continued with anisotropic temperature factors, first with unit weights and then with weights of the form: $w = 1/\{a_0t_0^*(x) + a_1t_1^*(x) \ldots a_nt_n(x)\}$, where a_i are coefficients of a Chebychev series in $t_i^*(x)$ with $x = F_o/F_o(\text{max.})$.

TABLE 1

Fractional atomic co-ordinates ($\times 10^4$, for S $\times 10^5$) with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
S(1)	62 544(7)	38 202(5)	21 197(7)
S(2)	57 065(7)	24 120(5)	51 535(6)
O(10)	6 909(2)	3 801(2)	2 991(2)
O(11)	6 607(3)	3 245(2)	1 486(2)
O(20)	5 557(2)	1 523(2)	5 539(2)
O(21)	6 607(2)	3 003(2)	5 548(2)
N(1)	4 991(2)	3 648(2)	2 149(2)
N(2)	5 840(2)	2 271(2)	4 164(2)
N(3)	3 667(2)	2 828(2)	2 638(2)
C(1)	3 726(2)	708(2)	4 016(2)
C(2)	2 635(3)	594(2)	4 021(3)
C(3)	1 875(3)	1 205(3)	3 541(3)
C(4)	2 215(3)	1 929(2)	3 069(2)
C(5)	3 319(2)	2 057(2)	3 085(2)
C(6)	4 093(2)	1 434(2)	3 561(2)
C(7)	4 682(2)	2 864(2)	2 474(2)
C(8)	2 932(3)	3 634(2)	2 386(3)
C(11)	6 163(3)	6 649(2)	2 003(3)
C(12)	6 231(3)	5 732(2)	2 321(2)
C(13)	6 189(2)	4 992(2)	1 739(2)
C(14)	6 026(3)	6 831(2)	1 122(3)
C(15)	6 005(3)	6 083(2)	554(3)
C(16)	6 086(3)	5 159(2)	862(2)
C(17)	5 894(4)	7 820(3)	770(4)
C(21)	4 494(3)	3 068(2)	5 084(2)
C(22)	4 398(3)	3 924(2)	4 655(2)
C(23)	3 484(3)	4 471(2)	4 624(2)
C(24)	2 647(3)	4 169(2)	5 010(2)
C(25)	2 739(3)	3 305(3)	5 412(3)
C(26)	3 655(3)	2 745(2)	5 456(2)
C(27)	1 680(4)	4 784(3)	4 998(3)
C(31)	5 290(2)	1 552(2)	3 524(2)
C(32)	5 947(2)	633(2)	3 654(2)
C(33)	5 568(3)	−84(2)	2 929(2)
C(34)	5 613(3)	350(2)	2 046(3)
C(35)	4 942(3)	1 258(2)	1 886(2)
C(36)	5 343(2)	1 964(2)	2 636(2)
H(11) *	4 287	273	4 351
H(21)	2 379	104	4 460
H(31)	1 041	1 022	3 496
H(41)	1 629	2 387	2 727
H(81)	3 329	4 170	2 328
H(82)	2 347	3 533	1 952
H(83)	2 559	3 785	2 778
H(111)	8 763	2 202	2 538
H(121)	6 270	5 616	2 924
H(151)	5 914	6 153	−133
H(161)	6 044	4 601	390
H(171)	5 206	7 974	553
H(172)	6 133	8 374	1 406
H(173)	6 534	8 060	461
H(201)	6 276	2 621	3 868
H(221)	4 981	4 151	4 421
H(231)	3 459	5 000	4 279
H(251)	2 205	3 142	5 710
H(261)	3 768	2 165	5 809
H(271)	1 474	4 944	4 511
H(272)	1 630	5 182	5 404
H(273)	1 119	4 481	5 273
H(321)	6 712	796	3 658
H(322)	5 950	378	4 247
H(331)	4 716	276	2 945
H(332)	6 025	655	3 058
H(341)	5 296	138	1 522
H(342)	6 346	480	2 025
H(351)	4 188	1 103	1 824
H(352)	5 027	1 588	1 431
H(361)	6 142	2 147	2 595

* U_{iso} for H atoms 0.05.

The parameters a_i were calculated before each cycle of refinement by least-squares, minimising $\Sigma(F_o - F_c)$[4] over all reflections. The final parameters were $a_0 = 41$, $a_1 = 57.6$, $a_2 = 31.9$, $a_3 = 21.4$, and $a_4 = 11.8$. The least-squares matrix was blocked into two parts, one containing the derivatives of the positional parameters and the second, those of the thermal parameters and scale factor. At R 0.073, a difference-Fourier synthesis revealed the positions of 29 hydrogen atoms, although the electron density was poorly defined about C(27) and C(17). The remaining two hydrogen atoms [H(172) and H(173)] were placed from a second difference-Fourier synthesis following a further cycle of refinement of the non-hydrogen atom parameters.

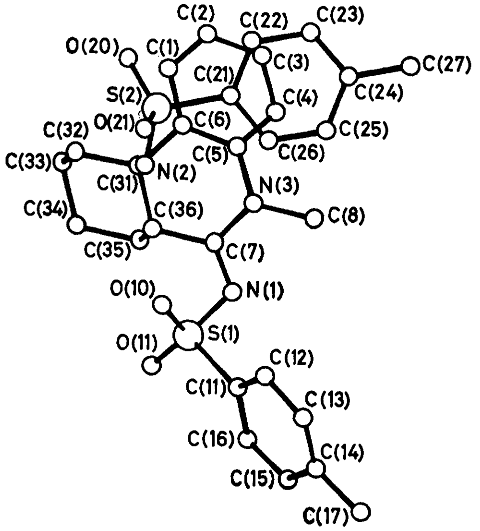


FIGURE 1 Generalised projection of the non-hydrogen atoms of the molecule of (2), showing the atom numbering system used in the analysis

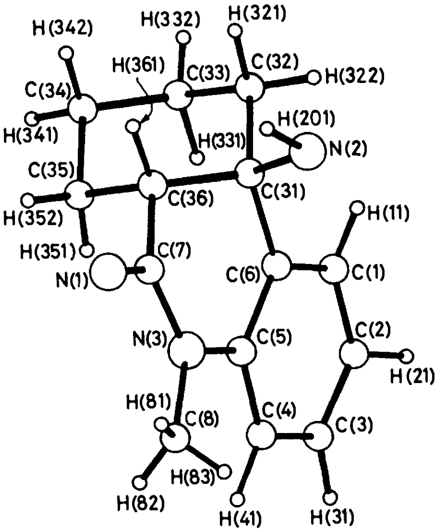


FIGURE 2 Projection down [111] of the phenanthridine residue of (2) (both p-tolylsulphonyl groups omitted)

Hydrogen atoms were incorporated in the model but not refined. Least-squares refinement converged at R 0.043.

All calculations were performed on the Oxford University Computing Laboratory's ICL 1906A using the CRYSTALS package of crystallographic programs.[9] Atomic scattering factors were taken from ref. 10. In the latter stages of refinement, allowance was made for the anomalous dispersion of sulphur.[11] Observed structure amplitudes, structure factors calculated from the final atomic parameters in Table 1, and thermal parameters, are listed in Supplementary Publication, SUP No. 22037 (30pp, 1 microfiche).*

TABLE 2

Bond lengths (Å) and interbond angles (°), with estimated standard deviations in parentheses

(*a*) Bond distances

S(1)–N(1)	1.610 (3)	C(6)–C(1)	1.385 (4)
S(1)–O(10)	1.437 (3)	C(6)–C(31)	1.520 (4)
S(1)–O(11)	1.424 (3)	C(7)–C(36)	1.513 (4)
S(1)–C(11)	1.764 (3)	C(11)–C(12)	1.385 (5)
S(2)–N(2)	1.606 (3)	C(12)–C(13)	1.390 (5)
S(2)–O(20)	1.428 (2)	C(13)–C(14)	1.379 (6)
S(2)–O(21)	1.436 (2)	C(14)–C(15)	1.383 (5)
S(2)–C(21)	1.763 (3)	C(14)–C(17)	1.504 (5)
N(1)–C(7)	1.315 (4)	C(15)–C(16)	1.394 (4)
N(2)–C(31)	1.494 (4)	C(16)–C(11)	1.373 (5)
N(3)–C(5)	1.416 (4)	C(21)–C(22)	1.382 (4)
N(3)–C(7)	1.349 (4)	C(22)–C(23)	1.374 (5)
N(3)–C(8)	1.469 (3)	C(23)–C(24)	1.383 (5)
C(1)–C(2)	1.377 (4)	C(24)–C(25)	1.373 (5)
C(2)–C(3)	1.387 (5)	C(24)–C(27)	1.489 (5)
C(3)–C(4)	1.384 (5)	C(25)–C(26)	1.384 (5)
C(4)–C(5)	1.388 (4)	C(26)–C(21)	1.380 (5)
C(5)–C(6)	1.405 (4)		
C(31)–C(32)	1.532 (4)	C(34)–C(35)	1.530 (4)
C(32)–C(33)	1.525 (5)	C(35)–C(36)	1.546 (4)
C(33)–C(34)	1.526 (5)	C(36)–C(31)	1.523 (4)

(*b*) Bond angles

O(10)–S(1)–O(11)	116.9(2)	C(12)–C(11)–C(16)	120.7(3)
O(10)–S(1)–N(1)	109.7(2)	C(11)–C(12)–C(13)	118.9(3)
O(11)–S(1)–N(1)	112.5(2)	C(12)–C(13)–C(14)	121.3(3)
O(10)–S(1)–C(11)	108.4(2)	C(13)–C(14)–C(15)	118.8(3)
O(11)–S(1)–C(11)	107.7(2)	C(13)–C(14)–C(17)	121.5(4)
N(1)–S(1)–C(11)	100.2(1)	C(15)–C(14)–C(17)	119.7(4)
O(20)–S(2)–O(21)	119.6(2)	C(14)–C(15)–C(16)	120.6(4)
O(20)–S(2)–N(2)	110.3(1)	C(15)–C(16)–C(11)	119.6(3)
O(21)–S(2)–N(2)	104.9(2)	S(2)–C(21)–C(22)	118.7(3)
O(20)–S(2)–C(21)	107.8(2)	S(2)–C(21)–C(26)	121.3(2)
O(21)–S(2)–C(21)	107.8(2)	C(22)–C(21)–C(26)	120.0(3)
N(2)–S(2)–C(21)	105.6(1)	C(21)–C(22)–C(23)	120.1(3)
S(1)–N(1)–C(7)	120.7(2)	C(22)–C(23)–C(24)	120.7(3)
S(2)–N(2)–C(31)	127.4(2)	C(23)–C(24)–C(25)	118.6(3)
C(5)–N(3)–C(7)	121.5(2)	C(23)–C(24)–C(27)	120.0(3)
C(5)–N(3)–C(8)	119.7(2)	C(25)–C(24)–C(27)	121.3(4)
C(7)–N(3)–C(8)	118.7(2)	C(24)–C(25)–C(26)	121.7(3)
C(2)–C(1)–C(6)	121.8(3)	C(25)–C(26)–C(21)	118.9(3)
C(1)–C(2)–C(3)	119.4(3)	N(2)–C(31)–C(32)	109.5(2)
C(2)–C(3)–C(4)	120.1(3)	N(2)–C(31)–C(36)	104.4(4)
C(3)–C(4)–C(5)	120.2(3)	N(2)–C(31)–C(6)	111.6(2)
C(4)–C(5)–C(6)	120.0(3)	C(6)–C(32)–C(32)	114.0(2)
C(4)–C(5)–N(3)	120.0(3)	C(6)–C(31)–C(36)	108.0(2)
C(6)–C(5)–N(3)	120.0(2)	C(32)–C(31)–C(36)	108.9(2)
C(1)–C(6)–C(5)	118.4(3)	C(31)–C(32)–C(33)	113.3(2)
C(1)–C(6)–C(31)	122.5(2)	C(32)–C(33)–C(34)	109.9(3)
C(5)–C(6)–C(31)	119.1(2)	C(33)–C(34)–C(35)	111.5(3)
N(1)–C(7)–C(36)	125.8(3)	C(32)–C(35)–C(36)	110.1(3)
N(1)–C(7)–N(3)	118.1(2)	C(31)–C(36)–C(7)	110.5(2)
N(3)–C(7)–C(36)	116.1(2)	C(31)–C(36)–C(35)	110.0(2)
S(1)–C(11)–C(12)	120.0(3)	C(7)–C(36)–C(35)	112.0(2)
S(1)–C(11)–C(16)	119.3(3)		

RESULTS AND DISCUSSION

Interatomic distances and interbond angles are given in Table 2 and certain torsion angles in Table 3.[5,12,13] The atom numbering corresponds to Figures 1 and 2.

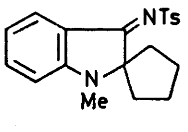
The crystals are built up from isolated molecules of formula (2) which neither make unduly short contacts with their neighbours nor form hydrogen bonds at the amino-nitrogen N(2).

Figure 2 demonstrates that the saturated ring junction at C(31) and C(36) is *cis*. The ring C(31)—(36) has the chair conformation, and C–C bond lengths and interbond angles have values expected for a cyclohexane-like system.

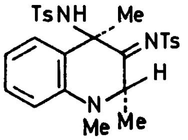
The dimensions of the *p*-tolylsulphonylamino-residue at C(31) agree very well with the corresponding values found in *N*-*p*-tolylsulphonylbenzylamine (9)[12] except that the angle C(31)–N(2)–S(2) is larger [127.3(2)°] than in (9) [119.5(4)°]. This is probably attributable to the steric interaction between the fused-ring system and the tolyl group which lies directly above it (see Figure 1). Smaller discrepancies are found in the bond lengths N(2)–S(2) [1.606 in (2) 1.619 Å in (1)] and C(31)–N(2) (1.494 and 1.475 Å). The former is only on the borders of significance (4σ) and the finding of one long bond to an sp^3 carbon atom bonded to four non-hydrogen atoms is not unusual. The dihedral angles about N(2)–S(2) are similar to those found in related sulphonylamino-systems (Table 3) and reflect the attraction between S–O and N–H dipoles of opposite polarity.

$PhCH_2NHTs$

(9)



(10)



(11)

The molecular environment of the *p*-tolylsulphonylimino group in (2) is very similar to that of the same residue in (7) but differs greatly from those in (10) and (11). However, in these four compounds the dimensions and conformation of the tolysulphonylimino-groups are quite similar. In *p*-tolylsulphonylimino-systems, although the $C–SO_2$ grouping closely resembles that in a *p*-tolylsulphonylamino-system, the angle N–S–C [100.2° in (2)] has an average value of 100° whereas it is larger, *ca.* 107°, in sulphonylamino-systems. The dihedral angles about S(1)–N(1) (Table 3) are very different from those in the sulphonylamino-group but are similar to those in other sulphonylimino-systems. They reflect the repulsion of the nitrogen lone-pair by the S–O dipoles.

---

* See note about Supplementary Publications in Notice to Authors No. 7, in *J.C.S. Perkin II*, 1975, Index issue.

[9] J. R. Carruthers, 'Crystals' User Manual, Oxford University Computing Laboratory, 1975.

[10] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A27**, 321.

[11] D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 1970, **53**, 1891.

[12] T. S. Cameron, K. Prout, B. Denton, R. Spagna, and E. White, *J.C.S. Perkin II*, 1975, 176.

[13] A. S. Bailey, P. A. Baldry, J. M. Peach, S. R. Critchley, K. Prout, and E. White, *J. Chem. Soc. Perkin I*, 1976, 2254.

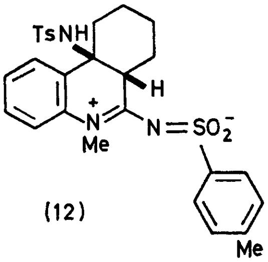
The orientation of the N–SO_2 group with respect to the plane of the tolyl group varies quite considerably in *p*-tolylsulphonylamino- and *p*-tolylsulphonylimino-systems (see Table 3). In (7), for both amino- and imino-nitrogens, one sulphonyl oxygen lies in the plane of the tolyl group and this is true for the sulphonylamino-group in (2). For the sulphonylimino-group in the latter, the plane of the tolyl residue appears to be at right angles to S(1)–N(1) as viewed down S(1)–C(21) such that O(10) and O(11) lie 0.63 and 0.45 Å out of the plane of the benzene ring, C(11)—(16), respectively. It would seem from an analysis of the compounds listed in Table 3 that the orientation of the N–SO_2 and tolyl groups with respect to each other is determined by crystal packing requirements.

TABLE 3

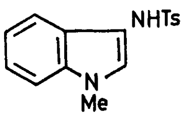
Selected torsion angles with values from related compounds for comparison. The torsion angle about the bond J–K is defined as the angle the bond K–L is rotated from the IJK plane. It is positive when on looking from IJ to KL the rotation is clockwise

Angle I–J–K–L	(2)	(7) [a]	(9) [b]	(10) [b]	(11) [b]	(13) [b]	(14) [c]
C(31)–N(2)–S(2)–O(20)	34.6	−43.7	−54.3	−8.5		51.7	21.9
C(31)–N(2)–S(2)–O(21)	164.7	−172.5	177.6	−138.7		179.5	151.1
C(7)–N(1)–S(1)–O(10)	−60.4	−50.8		−68.2	−56.4		
C(7)–N(1)–S(1)–O(11)	71.6	82.0		63.7	76.1		
S(1)–N(1)–C(7)–N(3)	167.5	−170.8					
N(1)–C(7)–N(3)–C(8)	4.6	−0.1					
N(1)–C(7)–N(3)–C(5)	−172.2	177.1					
C(7)–N(3)–C(5)–C(6)	16.4	1.5					
C(7)–N(3)–C(5)–C(4)	−165.1	−176.8					

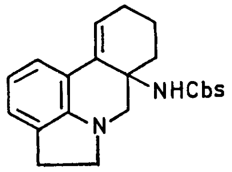
[a] Ref. 5. [b] Ref. 12. [c] Ref. 13.



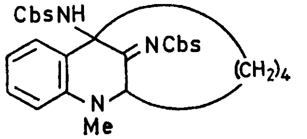
(12)



(13)



(14)



(15)

For the sulphonylimino-groups, the S–N bond lengths in the series of compounds (7), (2), (10), and (9) progressively increase from 1.553, 1.610, 1.619, to 1.646 Å. The longest bond, in (9), is where the C=N–SO_2 group is isolated from the neighbouring aromatic system by a saturated carbon atom. The short bond in (7) has been explained in terms of electron delocalisation involving forms such as (8). A similar form of (10) can be drawn but appears to be less significant. At first sight, the form (12) of (2) might be thought to make little contribution but on closer inspection the systems (2) and (7) are very alike. In both compounds they are near-planar (see Table 3) and the C–N double bond is almost 0.1 Å longer than in the isolated system in (11). Contributions from forms such as (8) and (12) will tend to deactivate the benzene ring of the indolene residue towards electrophilic substitution. Thus (2) and (7) are not brominated by $C_5H_5N^+HBr_3^-$ under vigorous conditions whereas, under similar conditions, (10) and (15) react very rapidly.

We thank the S.R.C. for a studentship for S. R. C.

[6/2138 *Received, 19th November, 1976*]