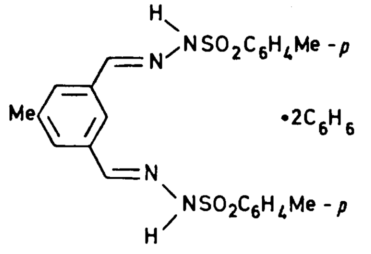
Crystal Structure of a 1 : 2 Channel Inclusion Adduct of 5-Methylbenzene-1,3-dicarbaldehyde Bis-(*p*-tolylsulphonylhydrazone) and Benzene

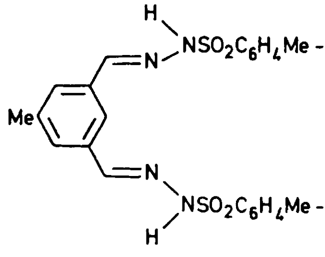
By **Tze-Lock Chan** and **Thomas C. W. Mak,*** Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong
James Trotter, Department of Chemistry, The University of British Columbia, Vancouver, B.C., Canada V6T 1W5

A 1 : 2 crystalline solvate (1) of 5-methylbenzene-1,3-dicarbaldehyde bis-(*p*-tolylsulphonylhydrazone) (2) and benzene has been synthesized and characterized as a channel inclusion complex by *X*-ray analysis. Crystals of (1) are orthorhombic, with a = 8.135(2), b = 19.021(4), c = 23.015(2) Å, Z = 4, and space group *C*2*ca* (No. 41). The structure was solved by direct methods and refined to R 0.039 on 1 211 observed diffractometer data. The bis-(tosylhydrazone) molecules (2) attain crystallographic two-fold symmetry and constitute the host lattice. The guest (benzene) molecules occupy positions in continuous, zigzag channels running through the crystal along the *a* direction, the axis of each channel coinciding with a crystallographic two-fold screw axis.

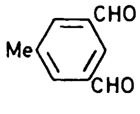
EVER since the elucidation of the nature of clathration by Palin and Powell[1] more than 30 years ago, research in inclusion chemistry has expanded enormously, particularly so recently, as shown by the appearance of several comprehensive reviews and monographs on molecular inclusion phenomena,[2,3] clathrate hydrates,[4] graphite intercalates,[5] transition metal dichalcogenides,[6] zeolite molecular sieves,[7] cyclodextrins,[8] crown compounds,[9] cryptates,[10] macrolides,[11] and cyclic peptides.[11] In practical applications, inclusion compounds have proved to be of great importance in the pharmaceutical industry [2,12] and in chemical separation and purification.[13]



(1)



(2)



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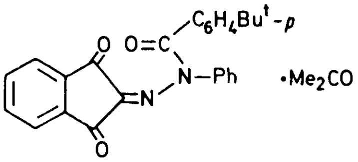

(4)

In the course of our studies in organo-sulphur chemistry, we prepared 5-methylbenzene-1,3-dicarbaldehyde (3) by the Sommelet reaction [14] of 1,3-bis(bromomethyl)-5-methylbenzene.[15a] Reaction of (3) with 4-methylbenzenesulphonohydrazide (2 mol. equiv.) gave, as expected, the bis(tosylhydrazone) (2). Crystallisation of (2) from benzene–methanol (7 : 3) yielded a stable, colourless compound (1) whose elemental analysis and ^{1}H n.m.r. spectrum could only be accounted for by the incorporation of 2 molar equivalents of benzene. The benzene in this molecular adduct is very firmly retained, with no detectable composition change when a sample was subjected to 50 °C under 10 mmHg for 12 h. However, left at room temperature for prolonged periods, the crystalline ' solvate ' (1) gradually decomposed owing to loss of ' solvent '. This behaviour is indicative of guest–host interaction and prompted us to undertake an *X*-ray crystallographic study.

EXPERIMENTAL

M.p.s were determined with a Koefler hot-stage apparatus. ^{1}H N.m.r. spectra (60 MHz) were recorded in $CDCl_3$ with a JEOL 60HL spectrometer using tetramethylsilane as internal standard. Elemental analyses of 5-methylbenzene-1,3-dicarbaldehyde and the bis(tosylhydrazone)–benzene 1 : 2 complex (1) were determined, respectively, by the Australian Microanalytical Service, Parkville, Victoria, and by the Chemistry Department of the Chinese University using a Hewlett-Packard 185 CHN analyser.

5-Methylbenzene-1,3-dicarbaldehyde (3).—To a rapidly stirred solution of hexamethylenetetramine (12.6 g, 0.1 mol) in chloroform (150 ml) was added 1,3-bis(bromomethyl)-5-methylbenzene [15a] (11.2 g, 0.04 mol) in one portion. An exothermic reaction commenced within a few minutes giving a finely dispersed white precipitate. The resulting mixture was further refluxed for 1 h and then left at 0 °C for 3 h. The hexamethylenetetramine salt was then filtered off, washed with chloroform, and dried *in vacuo*. After decomposition of this material in boiling 10% acetic acid (200 ml) for 1 h, the product was separated by steam distillation. Recrystallisation of the crude material from aqueous ethanol afforded pure 5-*methylbenzene*-1,3-*dicarbaldehyde* (3) (3.0 g, 50%) as needles, m.p. 92—93 °C (lit.,[15b] 96—97 °C) (Found: C, 73.1; H, 5.4. Calc. for $C_9H_8O_2$: C, 73.0; H, 5.4%); τ 7.50 (3 H, s, Me), 1.93 (2 H, s, 4- and 6-H), 1.74 (1 H, s, 2-H), and 0.29 (2 H, s, aldehydic H).

5-*Methylbenzene*-1,3-*dicarbaldehyde Bis*-(p-*tolylsulphonylhydrazone*) (2)–*Benzene* 1 : 2 *Complex* (1).—To a boiling solution of 4-methylbenzenesulphonohydrazide (7.5 g, 0.04 mol) in methanol (50 ml) was added dropwise over 0.5 h a solution of 5-methylbenzene-1,3-dicarbaldehyde (3.0 g, 0.02 mol) in methanol (40 ml). After further heating for 0.5 h, the solvent was removed *in vacuo*. Two crystallisations of the residue from benzene–methanol (7 : 3) followed by drying at 40 °C and 10 mmHg for 10 h afforded the *bis*(*tosylhydrazone*)–*benzene* 1 : 2 *solvate* (1) (5.3 g, 41%) as prisms, m.p. 117—119 °C (decomp.) (Found: C, 65.6; H, 5.6; N, 8.7. $C_{23}H_{24}N_4O_4S_2 \cdot 2C_6H_6$ requires: C, 65.5; H, 5.7; N, 8.7%); τ 7.95 (3 H, s, Ar-5-Me), 7.76 (6 H, s, Ar-4′-Me), 2.15—2.98 (25 H, group of multiplets including a sharp singlet at 2.75, ArH, N=CH, and C_6H_6 protons), and 1.15 (2 H, broad s, exchangeable with D_2O, NH). Upon exposure to air, the solvate crystals gradually turned opaque and finally sintered into yellowish fragments in about a month. However, it was found that samples stored in stoppered vials could be kept at room temperature for six months without deterioration.

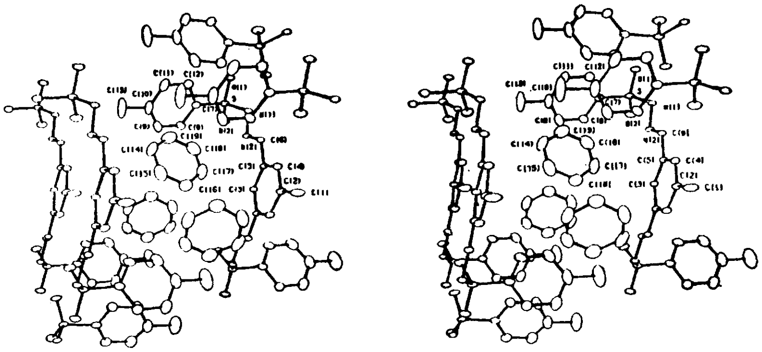

FIGURE 1 Stereoview of the 1 : 2 adduct looking along a channel parallel to the *a* axis. The *b* and *c* axes point to the right and upward respectively. Atom numbering of asymmetric unit corresponds to that of Table 1, and hydrogen atoms have been omitted for the sake of clarity.

For the solvent-free bis(tosylhydrazone) (2), the ^1H n.m.r. spectrum gave signals at τ 8.02 (3 H, s, Ar-5-Me), 7.78 (6 H, s, Ar-4′-Me), 2.66—3.05 (2 H, m, N=CH), 2.00—2.45 (11 H, m, ArH), and 0.90 br. (2 H, s, exchangeable with D_2O, NH). Addition of a small amount of benzene to the n.m.r. sample yielded a sharp singlet at τ 2.75.

X-*Ray Structure Determination of the Bis*(*tosylhydrazone*)–*Benzene* 1 : 2 *Solvate* (1).—X-Ray photographs showed that the crystals are elongated along *a* and well developed on the {010} and {001} faces.

Crystal Data.—$C_{23}H_{24}N_4O_4S_2 \cdot 2C_6H_6$, $M = 640.84$. Orthorhombic, $a = 8.135(2)$, $b = 19.021(4)$, $c = 23.015(2)$ Å, $U = 3561$ Å^3, $D_m = 1.205(5)$ g cm^{-3} (by flotation in aqueous KI), $Z = 4$ (for 1 : 2 solvate), $D_c = 1.195$ g cm^{-3}. Mo-K_α radiation, $\lambda = 0.71068$ Å, μ(Mo-K_α) = 1.91 cm^{-1}. Systematic absences: *hkl* with $(h + k)$ odd, *h0l* with *l* odd, and *hk0* with *h* odd; space group *C2ca* (No. 41, interchange of *a* and *c* axes transforms it to *Aba2* as described in ref. 16).

Intensity data were collected on a crystal with dimensions *ca.* 0.5 × 0.4 × 0.3 mm on an Enraf Nonius CAD-4 diffractometer with graphite monochromator and Mo-K_α radiation. A variable speed ω scan over a range of $r = (0.85 + 0.35 \tan\theta)$ degrees in ω was employed. The scan was extended at both ends by $r/4$ for background measurement. Crystal orientation was monitored every 100 reflections. The intensities of three standard reflections, checked hourly throughout the data collection, fluctuated within ±2% and showed no systematic net loss of intensity. Of the 2 771 unique reflections measured up to $2\theta < 60°$, 1 211 (43.7%) were considered observed at the $3\sigma(I)$ significance level, where $\sigma^2(I) = S + B + (0.04S)^2$, with S = scan count and B = normalized background count. No absorption correction was applied. After data collection the crystal remained clear and there was no visual evidence of deterioration.

Normalized structure factors (E) in parity groups *ggg* and *uuu* were much stronger than those in parity groups *ggu* and *uug*. The structure was solved with MULTAN[17] after renormalization of the E values. The most promising E map calculated with 405 assigned phases yielded peaks for 13 atoms in the bis(tosylhydrazone) molecule. Successive cycles of structure-factor and Fourier calculations revealed all 24 non-hydrogen atoms in the asymmetric unit. Further anisotropic least-squares refinement followed by a difference map showed most of the hydrogen atoms. The remaining hydrogen atoms were introduced at their calculated positions, and each hydrogen atom was assigned an isotropic thermal parameter commensurately larger than that of the atom to which it is bonded. At the end of the refinement, R converged to 0.039 for 1 211 observed reflections. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, with $w = 1/\sigma^2(F_o)$. Scattering factors for non-hydrogen[18] and spherically bonded hydrogen atoms[19] were generated from the coefficients of analytical approximations.

The numbering of the atoms in the asymmetric unit is shown in Figure 1, and the final positional parameters appear in Table 1. Bond distances and angles are listed in Table 2. Thermal parameters, positions of hydrogen atoms, and comparison of observed and calculated structure factors are available as Supplementary Publication No. SUP 22673 (28 pp.).*

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* For details, see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1979, Index issue.

Table 1

Positional parameters (fractional, S × 10^5; O, N, C × 10^4) with estimated standard deviations in parentheses

	x	*y*	*z*
(a) Asymme tric unit of host framework			
S	0	48 955(4)	19 584(2)
O(1)	−127(4)	5 089(1)	2 559(1)
O(2)	−1 219(3)	5 116(2)	1 564(1)
N(1)	1 756(3)	5 245(1)	1 758(1)
N(2)	2 212(3)	5 107(1)	1 179(1)
C(1)	8 939(6)	$\frac{1}{2}$	0
C(2)	7 089(5)	$\frac{1}{2}$	0
C(3)	3 624(5)	$\frac{1}{2}$	0
C(4)	6 206(4)	5 110(2)	506(1)
C(5)	4 502(3)	5 103(2)	514(1)
C(6)	3 731(3)	5 191(1)	1 084(1)
C(7)	211(4)	3 987(2)	1 915(1)
C(8)	−437(7)	3 633(2)	1 458(1)
C(9)	−299(11)	2 917(3)	1 438(3)
C(10)	492(10)	2 543(3)	1 846(3)
C(11)	1 128(9)	2 900(3)	2 332(3)
C(12)	989(6)	3 625(2)	2 366(2)
C(13)	626(17)	1 749(4)	1 836(4)
(b) Guest molecule			
C(14)	5 454(12)	1 862(4)	897(4)
C(15)	6 332(11)	1 938(5)	409(5)
C(16)	6 467(12)	2 572(7)	155(3)
C(17)	5 762(12)	3 125(4)	419(5)
C(18)	4 929(15)	3 050(5)	901(5)
C(19)	4 771(13)	2 426(7)	1 135(3)

Table 2

Bond lengths (Å) and angles (°) and their e.s.d.s

(a) Host molecule			
C(1)–C(2)	1.505(6)	S–O(2)	1.408(2)
C(2)–C(4)	1.384(4)	S–C(7)	1.739(4)
C(4)–C(5)	1.386(4)	C(7)–C(8)	1.356(4)
C(5)–C(3)	1.397(3)	C(8)–C(9)	1.368(7)
C(5)–C(6)	1.464(3)	C(9)–C(10)	1.343(9)
C(6)–N(2)	1.265(4)	C(10)–C(11)	1.407(9)
N(2)–N(1)	1.407(3)	C(11)–C(12)	1.386(7)
N(1)–S	1.642(2)	C(12)–C(7)	1.397(5)
S–O(1)	1.435(2)	C(10)–C(13)	1.515(9)
C(1)–C(2)–C(4)	121.2(2)	O(1)–S–O(2)	119.6(2)
C(2)–C(4)–C(5)	121.9(3)	O(1)–S–C(7)	108.5(1)
C(4)–C(5)–C(3)	120.1(3)	O(2)–S–C(7)	109.2(2)
C(5)–C(3)–C(5)^i	118.5(3)	S–C(7)–C(8)	120.0(3)
C(4)–C(2)–C(4)^i	117.5(4)	S–C(7)–C(12)	119.4(3)
C(4)–C(5)–C(6)	116.1(2)	C(7)–C(8)–C(9)	119.3(5)
C(3)–C(5)–C(6)	123.8(2)	C(8)–C(9)–C(10)	122.9(6)
C(5)–C(6)–N(2)	124.0(2)	C(9)–C(10)–C(11)	118·5(5)
C(6)–N(2)–N(1)	113.4(2)	C(10)–C(11)–C(12)	119.7(5)
N(2)–N(1)–S	114.8(2)	C(11)–C(12)–C(7)	119.0(4)
N(1)–S–O(1)	103.3(1)	C(12)–C(7)–C(8)	120.6(4)
N(1)–S–O(2)	108.1(1)	C(9)–C(10)–C(13)	123.5(8)
N(1)–S–C(7)	107.5(1)	C(11)–C(10)–C(13)	117.8(8)
(b) Guest molecule			
C(14)–C(15)	1.349(10)	C(14)–C(15)–C(16)	120.4(7)
C(15)–C(16)	1.345(11)	C(15)–C(16)–C(17)	118.1(7)
C(16)–C(17)	1.344(11)	C(16)–C(17)–C(18)	121.3(8)
C(17)–C(18)	1.309(11)	C(17)–C(18)–C(19)	119.9(8)
C(18)–C(19)	1.309(11)	C(18)–C(19)–C(14)	121.5(9)
C(19)–C(14)	1.327(11)	C(19)–C(14)–C(15)	118.8(7)

Superscript *i* refers to equivalent position *x*, 1 − *y*, −*z*.

RESULTS AND DISCUSSION

The present analysis confirmed the stoicheiometry of the 1 : 2 solvate (1). The structure of the bis(tosylhydrazone) molecule (2) is depicted in Figure 1, and the bond lengths and angles are listed in Table 2. The dimensions of the tosyl group are in close agreement with those in other tosyl compounds.[20] The measured geometry, as well as the proton positions directly located from the difference map, firmly established the hydrazone structure of (2) and ruled out the diazine formulation $-CH_2-N=N-$tosyl.

The bis(tosylhydrazone) molecule (2) retains its idealized C_2 molecular symmetry, with the crystallographic diad passing through atoms C(1)—C(3) (Figure 1). Atoms C(1)—C(6) of the central carbon skeleton are co-planar, as are C(7)—C(13) and S of the tosyl group, and the stereochemistry about the N(1)–S single bond is such that these two planar units make a dihedral angle of 80°. Packing of the large molecules (2) gives rise to infinite, zigzag channels running parallel to the *a* axis (Figures 1 and 2), the axis of each channel coinciding with a crystallographic two-fold screw axis. As can be seen from Figure 1, the flat and zigzag portions of a channel are bounded by the 5-methylbenzene-1,3-dicarbaldehyde bishydrazone and tosyl groups respectively. The channel width is *ca.* 9.5 Å if the host atoms are considered to constitute the boundary; the space available for guest accommodation thus has a cross-sectional diameter of (9.5 − 3.3) = 6.2 Å, comparable to the cavity sizes in several principal types of inclusion complexes.[21]

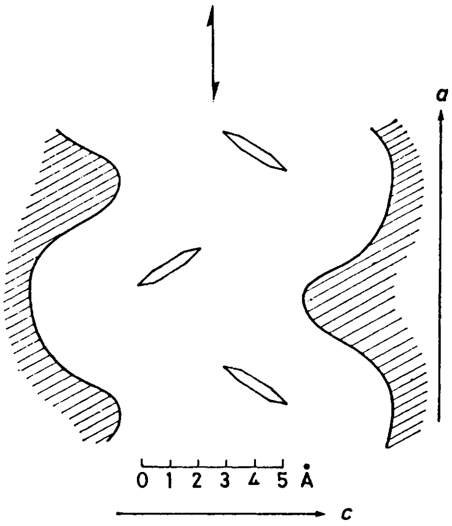

Figure 2 Schematic representation of a section parallel to (010) and through the walls of the host channel. Neighbouring guest molecules are related by the two-fold screw axis in the channel direction.

In contrast to the disorder of benzene guest molecules trapped in some phosphonitrilic trimer (cyclotriphosphazene) channel systems,[22] the benzene molecule in the present structure occupies a fixed position within the channel. The measured bond distances in the benzene guest molecule (Table 2) appear abnormally short as a consequence of the large thermal motion of atoms C(14)—C(19). No correction for libration was made as an analysis in terms of translation, libration, and screw tensors [23] did not yield a physically reasonable set of rigid-body thermal parameters. Figure 2 shows schematically that neighbouring guest molecules are related by the 2_1 axis in the *a* direction, and that the mode of packing makes efficient use of the turns in the channel. This snug fitting of channel space by guest molecules accounts mainly for the high degree of molecular order and the relative stability of the solvate.

Attempts to prepare similar adducts with toluene and pyridine as guests have failed, but we have yet to carry out a systematic study of the incorporation of other small molecules into the present host lattice. The fact that indanetrione 2-(*N*-*p*-t-butylbenzoyl-*N*-phenylhydrazone) has been found to form a 1 : 1 channel adduct (4) with acetone[21] strongly suggests that aryl hydrazones and related compounds should be more thoroughly investigated in the search for new inclusion compounds. Furthermore, with the wide recognition that trigonal symmetry is a dominant structural feature in many host molecules forming clathration lattices consolidated by van der Waals' attraction and/or hydrogen bonding,[3] the utilization of C_2 molecular symmetry, as found in the present adduct, seems worthy of consideration in further work directed towards the design and synthesis of novel host materials.

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