

C(4)–C(5), C(3)–C(4)–C(25), S–C(5)–C(4), C(6)–C(5)–C(4) are close to 120° indicate sp^2 bonding for C(2), C(3), C(4) and C(5). The S–C(1) bond length is normal but S–C(5) is a partial double bond. These results agree quite well with those obtained by Smith *et al.* (1972) for their thiopyran compound.

The non-planarity of the thiopyran ring is evident from Table 5 where the results of the best least-squares planes passing through the atoms in the thiopyran ring are given. The thiopyran ring has an almost 'boat shaped' conformation in which C(1) and C(4) are the out-of-the-plane atoms, being 0.523 and 0.119 Å respectively from the least-squares plane passing through C(2), C(3), C(5) and S.

The three aromatic rings are all planar and the bond

lengths and angles are normal. The dihedral angles of the phenyl rings at C(1) and C(5) and of the benzyl ring at C(2) are 87.9°, 47.0° and 64.9° respectively to plane III of Table 5.

The structure of the molecule with its environment when viewed along [100] is shown in Fig. 2. All the intermolecular distances are normal.

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Table 5. Displacements (Å) of atoms of the thiopyran ring from the least-squares best planes

| | Plane I through | Plane II through | Plane III through |
|------|-----------------------|---------------------|----------------------|
| | C(1)C(2)C(3)C(4)C(5)S | C(2)C(3)C(4)C(5) | C(2)C(3)C(5)S |
| C(1) | 0.2706 | 0.4655 | 0.5234 |
| C(2) | -0.1254 | 0.0366 | 0.0555 |
| C(3) | -0.1140 | -0.0745 | -0.0606 |
| C(4) | 0.1476 | 0.0738 | 0.1188 |
| C(5) | 0.0354 | -0.0360 | 0.0483 |
| S | -0.2141 | -0.1425 | -0.0431 |

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The Crystal and Molecular Structure of 2,4,6-Trimethyldiphenyl Sulphone (Phenyl Mesityl Sulphone)

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Crystals of 2,4,6-trimethyldiphenyl sulphone are orthorhombic, space group $Pn2_1a$, with eight molecules in the unit cell of dimensions $a=16.103$, $b=21.164$, $c=7.937$ Å. The structure was solved by direct methods using 2186 independent reflexions collected on a computer-controlled, four-circle Hilger and Watts diffractometer. It was refined by full-matrix least-squares calculations to a final R index of 0.046 for 1467 observed reflexions and 0.051 (weighted) for all the reflexions. Both molecules in the asymmetric unit are related by an almost exact centre of symmetry which does not coincide with any crystallographic centre of symmetry. Steric interactions between the sulphone and methyl groups lead to some abnormal bond lengths and angles.

Introduction

2,4,6-Trimethyldiphenyl sulphone, $C_6H_5 \cdot C_6H_2(CH_3)_3 \cdot SO_2$, usually called phenyl mesityl

sulphone, is a very unstable compound chemically (Holt & Pagdin, 1961). This chemical instability is no doubt closely linked to strain in the molecule caused by steric interactions between the sulphone and methyl groups. The crystal structure analysis has been carried out to investigate the nature of these strains. An X-ray examination of a similar unstable compound, dimesityl

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sulphone, was reported earlier (Chawdhury & Hargreaves, 1971) and evidence of extensive strain was found therein.

Experimental

2,4,6-Trimethyldiphenyl sulphone, obtained by oxidation of 2,4,6-trimethyldiphenyl sulphide (Holt & Pagdin, 1960), was recrystallized from ethanol, and orthorhombic needles elongated along *c* were obtained. The cell parameters (refined by least-squares fit to 20 reflexions measured on the diffractometer), with estimated limits of error, are: $a = 16.103 \pm 0.007$, $b =$

21.164 ± 0.008 and $c = 7.937 \pm 0.003$ Å. $D_m = 1.27$, $D_c = 1.276$ g cm⁻³ with 8 molecules in the unit cell.

The intensities of 2186 independent reflexions were measured on a computer-controlled Hilger and Watts four-circle diffractometer with Mo $K\alpha$ radiation; 719 of these were regarded as unobserved ($I < 2.5\sigma$). No correction for absorption was applied but it is estimated that errors thereby introduced represent less than 4% of $|F_o|$. Systematic absences were consistent with space group $Pnma$ or $Pn2_1a$. The intensity statistics (Table 1) did not unambiguously identify the space group.

Determination and refinement of the structure

The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971), assuming the space group $Pn2_1a$ with two molecules in the asymmetric unit. The correct solution showing the positions of 34 non-hydrogen atoms out of 36 was found from the sets of phases (300 E 's and 4000 Σ_2 relationships) with the highest combined figure of merit (2.70).

Table 1. Statistical averages and distribution of $|E|$ (Karle, Dragonette & Brenner, 1965)

| | Experimental | Centro-symmetric | Non-centro-symmetric |
|-----------------------------|--------------|------------------|----------------------|
| $\langle E^2 - 1 \rangle$ | 0.854 | 0.968 | 0.736 |
| $\langle E \rangle$ | 0.833 | 0.798 | 0.886 |
| % $ E > 3$ | 0.2 | 0.3 | 0.0 |
| % $ E > 2$ | 3.3 | 4.6 | 1.8 |
| % $ E > 1$ | 33.2 | 31.7 | 36.8 |

Table 2. Fractional positional parameters of non-hydrogen atoms and their estimated standard deviations ($\times 10^4$)

| Molecule A | <i>x</i> | <i>y</i> | <i>z</i> |
|------------|----------|-----------|------------|
| S | 6750 (1) | 1080 | 2174 (3) |
| O(1) | 7063 (3) | 1649 (3) | 1432 (6) |
| O(2) | 7183 (5) | 836 (3) | 3671 (6) |
| C(1) | 5724 (5) | 1237 (4) | 2785 (10) |
| C(2) | 5093 (5) | 1225 (4) | 1560 (9) |
| C(3) | 4275 (4) | 1403 (3) | 2053 (9) |
| C(4) | 4144 (5) | 1593 (4) | 3632 (9) |
| C(5) | 4773 (4) | 1599 (5) | 4862 (9) |
| C(6) | 5574 (5) | 1413 (4) | 4421 (9) |
| C(7) | 6691 (5) | 461 (4) | 629 (9) |
| C(8) | 6921 (5) | 578 (4) | -1065 (10) |
| C(9) | 6938 (5) | 66 (4) | -2164 (9) |
| C(10) | 6707 (5) | -542 (4) | -1634 (10) |
| C(11) | 6447 (5) | -627 (4) | 0 (10) |
| C(12) | 6446 (5) | -132 (4) | 1170 (9) |
| C(13) | 7165 (5) | 1212 (4) | -1808 (10) |
| C(14) | 6699 (5) | -1080 (4) | -2843 (10) |
| C(15) | 6145 (5) | -275 (4) | 2911 (10) |
| Molecule B | | | |
| S' | 5783 (1) | 3060 (1) | 7783 (3) |
| O(1') | 5484 (3) | 2486 (3) | 8547 (6) |
| O(2') | 5363 (3) | 3278 (3) | 6297 (6) |
| C(1') | 6845 (5) | 2911 (4) | 7194 (9) |
| C(2') | 7451 (5) | 2940 (4) | 8445 (10) |
| C(3') | 8262 (4) | 2770 (4) | 7968 (10) |
| C(4') | 8420 (5) | 2577 (4) | 6342 (9) |
| C(5') | 7800 (4) | 2536 (4) | 5134 (9) |
| C(6') | 6996 (4) | 2716 (4) | 5625 (9) |
| C(7') | 5828 (5) | 3666 (4) | 9283 (10) |
| C(8') | 5607 (4) | 3571 (4) | 10967 (9) |
| C(9') | 5606 (5) | 4087 (4) | 12080 (9) |
| C(10') | 5796 (5) | 4696 (4) | 11527 (10) |
| C(11') | 6049 (4) | 4763 (4) | 9873 (9) |
| C(12') | 6073 (5) | 4277 (4) | 8714 (10) |
| C(13') | 5378 (5) | 2951 (4) | 11795 (10) |
| C(14') | 5680 (5) | 5289 (5) | 12696 (10) |
| C(15') | 6351 (5) | 4432 (4) | 6953 (10) |

Table 3. U_{ij} 's of the form $\exp(-2\pi^2 \sum U_{ij} h_i h_j a_i^* a_j^*)$ with standard deviations ($\times 10^3$ Å)

| Molecule A | U_{11} | U_{22} | U_{33} | U_{12} | U_{13} | U_{23} |
|------------|----------|----------|----------|----------|----------|----------|
| S | 38 (1) | 59 (3) | 64 (1) | 0 (3) | 7 (1) | -3 (2) |
| O(1) | 56 (4) | 70 (5) | 82 (5) | -14 (3) | 6 (3) | -3 (2) |
| O(2) | 47 (4) | 102 (5) | 66 (4) | 14 (3) | -13 (3) | -12 (3) |
| C(1) | 26 (4) | 57 (7) | 69 (5) | 10 (3) | -5 (3) | -2 (3) |
| C(2) | 51 (5) | 63 (7) | 93 (8) | 0 (3) | -1 (4) | -11 (6) |
| C(3) | 31 (5) | 68 (7) | 110 (7) | 3 (5) | -12 (5) | -29 (7) |
| C(4) | 43 (5) | 54 (7) | 106 (7) | 5 (3) | 3 (4) | -5 (4) |
| C(5) | 76 (7) | 73 (7) | 76 (6) | 15 (5) | 24 (5) | 8 (5) |
| C(6) | 61 (5) | 68 (7) | 51 (6) | 10 (5) | 13 (4) | 8 (4) |
| C(7) | 42 (4) | 50 (5) | 52 (5) | 0 (3) | -3 (3) | 2 (3) |
| C(8) | 41 (4) | 65 (7) | 59 (6) | 2 (3) | -13 (4) | 2 (3) |
| C(9) | 58 (5) | 88 (9) | 62 (5) | 0 (2) | -2 (4) | 8 (5) |
| C(10) | 59 (5) | 70 (7) | 65 (7) | 5 (5) | 1 (4) | 8 (5) |
| C(11) | 59 (5) | 61 (5) | 73 (5) | 10 (3) | 2 (4) | 11 (4) |
| C(12) | 50 (4) | 54 (5) | 60 (5) | 7 (4) | -2 (3) | -9 (4) |
| C(13) | 104 (8) | 59 (7) | 72 (7) | -14 (5) | -5 (5) | 9 (6) |
| C(14) | 108 (9) | 45 (7) | 112 (9) | 19 (5) | -19 (7) | 11 (7) |
| C(15) | 112 (8) | 63 (5) | 69 (6) | -20 (5) | 5 (6) | -3 (6) |
| Molecule B | | | | | | |
| S' | 33 (1) | 70 (2) | 65 (2) | 0 (3) | -1 (1) | -12 (2) |
| O(1') | 50 (4) | 63 (5) | 96 (5) | -15 (3) | 13 (3) | -7 (4) |
| O(2') | 51 (4) | 102 (7) | 69 (4) | 10 (3) | 18 (3) | -10 (4) |
| C(1') | 29 (4) | 54 (9) | 65 (6) | -3 (5) | 1 (4) | 3 (5) |
| C(2') | 45 (5) | 77 (7) | 73 (6) | 5 (5) | -13 (5) | -8 (5) |
| C(3') | 66 (5) | 61 (7) | 96 (7) | 2 (5) | -1 (5) | 12 (7) |
| C(4') | 45 (7) | 81 (9) | 118 (8) | 0 (5) | 17 (6) | 3 (6) |
| C(5') | 51 (5) | 82 (7) | 85 (6) | 7 (5) | 12 (5) | -2 (5) |
| C(6') | 52 (5) | 75 (7) | 73 (6) | -3 (5) | -4 (4) | 24 (5) |
| C(7') | 41 (4) | 61 (7) | 60 (5) | 5 (4) | -5 (4) | -2 (5) |
| C(8') | 45 (5) | 50 (5) | 70 (6) | 5 (3) | -8 (4) | 7 (5) |
| C(9') | 68 (6) | 61 (7) | 69 (6) | 7 (7) | -6 (5) | -6 (5) |
| C(10') | 77 (7) | 59 (7) | 83 (7) | 12 (5) | -21 (5) | -23 (7) |
| C(11') | 59 (5) | 66 (4) | 87 (7) | 12 (5) | -5 (4) | 2 (4) |
| C(12') | 47 (4) | 63 (4) | 70 (7) | -3 (3) | -3 (4) | 8 (5) |
| C(13') | 88 (8) | 70 (9) | 73 (7) | -17 (7) | -5 (5) | 1 (5) |
| C(14') | 93 (9) | 104 (11) | 102 (11) | 9 (7) | 1 (5) | -3 (7) |
| C(15') | 81 (8) | 106 (11) | 80 (7) | 12 (7) | 32 (7) | 30 (8) |

Refinement began with an agreement index, R , of 0.28 for all 1487 observed reflexions. Five cycles of least-squares refinement using a weighting scheme of Cruickshank (1961) and anisotropic temperature factors for all non-hydrogen atoms reduced R to 0.09. H atoms, which were assigned isotropic temperature factors, were then included in the calculations and after six cycles of refinement, when the parameter shifts were less than one-quarter of the estimated standard deviations, final R indices of 0.046 (weighted), 0.054 (unweighted) for all the observed reflexions and 0.051 (weighted), 0.087 (unweighted) for the total number of reflexions were obtained.

The final positional and thermal parameters of non-hydrogen atoms of the two independent molecules (A

and B) are given in Tables 2 and 3. The parameters of the H atoms are given in Table 4.*

Description of the structure

Fig. 1 gives the dimensions of the two independent molecules deduced from the atomic coordinates. The estimated standard deviations are given within parentheses, calculated using the formula of Darlow (1960).

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31290 (12 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

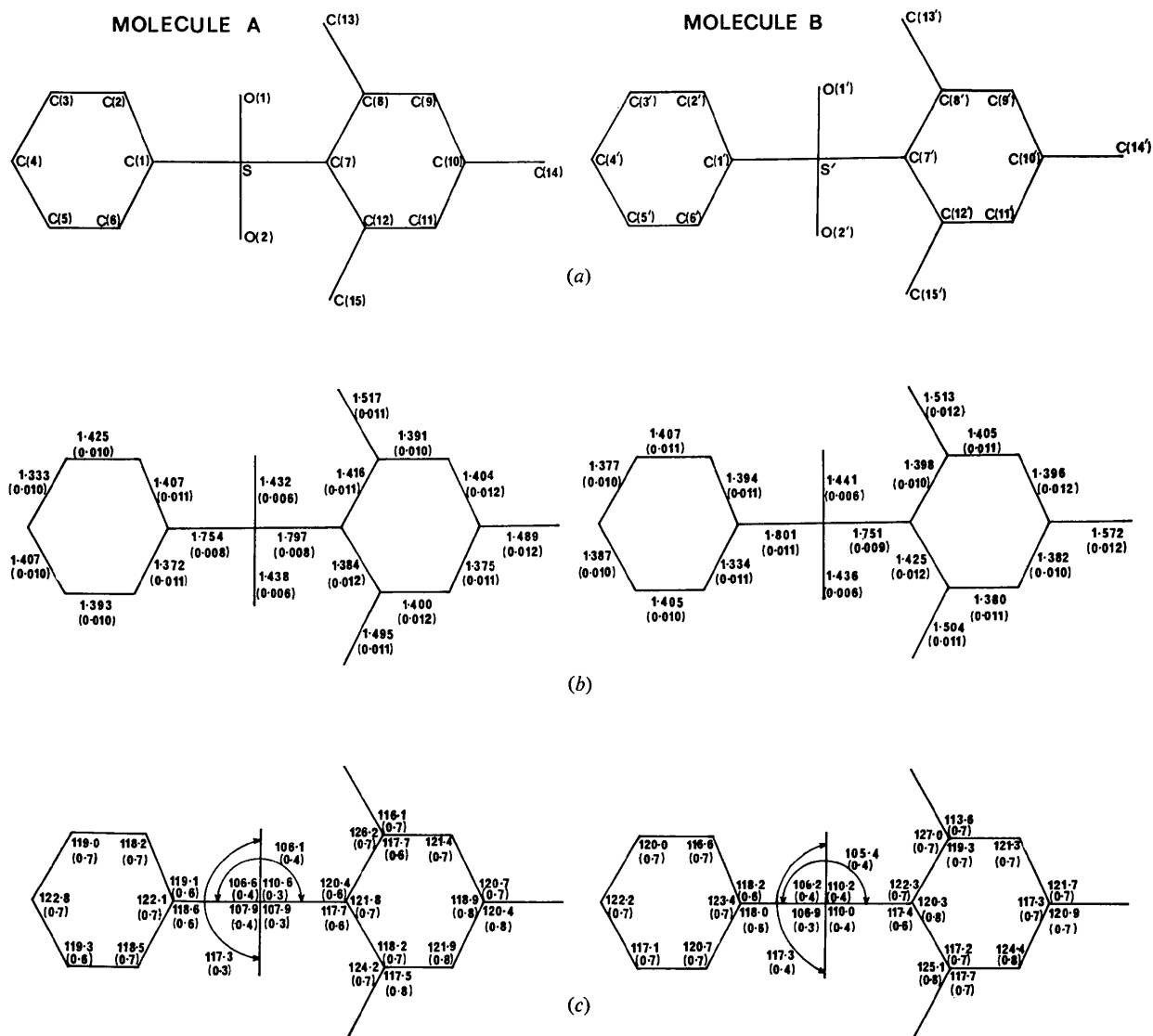


Fig. 1. Dimensions of phenyl mesityl sulphone. (a) Numbering of the atoms. (b) Bond lengths with standard deviations (Å). (c) Bond angles with standard deviations (°).

Fig. 2 shows the structure viewed along [001] and indicates all distances less than 3.8 Å between atoms of two independent molecules as well as neighbouring molecules; the intermolecular distances are quite normal except C(14')-C(5) = 3.46 Å.

Both independent molecules (*A* and *B*) have almost the same stereochemistry, although there are small differences in detail, and are related by an almost exact centre of symmetry which does not coincide, however, with any crystallographic centre of symmetry. The presence of this pseudo-centre of symmetry explains the ambiguous results obtained from the intensity statistics.

The sulphone groups for both the molecules are involved in steric interactions with the methyl groups attached to C(8), C(12), C(8') and C(12') and strains are indicated in Fig. 1(c) where the bond angles C(7)-C(8)-C(13), C(7)-C(12)-C(15), C(7')-C(8')-C(13') and C(7')-C(8')-C(15') are all more than 4° greater than the normal 120°; at each angle the methyl groups have been forced away from the sulphone group. The an-

Table 4. Final coordinates ($\times 10^3$) and isotropic temperature factors ($\text{Å}^2 \times 10^2$) of hydrogen atoms

Estimated standard deviations are in parentheses. Hydrogen atoms are given the same number as the carbon atoms to which they are bonded. The three hydrogen atoms of the methyl groups are distinguished by the letters *a*, *b* and *c*.

| Molecule <i>A</i> | <i>x</i> | <i>y</i> | <i>z</i> | U_{iso} |
|-------------------|----------|----------|-----------|------------------|
| H(2) | 529 (5) | 113 (3) | 28 (9) | 545 |
| H(3) | 387 (5) | 136 (4) | 106 (9) | 444 |
| H(4) | 359 (6) | 181 (4) | 408 (8) | 578 |
| H(5) | 470 (6) | 166 (5) | 622 (10) | 596 |
| H(6) | 602 (5) | 129 (3) | 528 (8) | 395 |
| H(9) | 707 (5) | 18 (4) | -339 (9) | 332 |
| H(11) | 617 (6) | -98 (5) | 44 (10) | 460 |
| H(8 <i>a</i>) | 700 (6) | 124 (5) | -310 (11) | 531 |
| H(8 <i>b</i>) | 776 (6) | 135 (5) | -148 (12) | 577 |
| H(8 <i>c</i>) | 688 (6) | 163 (5) | -151 (12) | 457 |
| H(10 <i>a</i>) | 728 (7) | -99 (5) | -264 (13) | 592 |
| H(10 <i>b</i>) | 619 (7) | -108 (5) | -355 (14) | 584 |
| H(10 <i>c</i>) | 634 (6) | -144 (5) | -237 (10) | 534 |
| H(12 <i>a</i>) | 643 (7) | -5 (5) | 386 (13) | 592 |
| H(12 <i>b</i>) | 636 (8) | -69 (7) | 298 (13) | 516 |
| H(12 <i>c</i>) | 580 (7) | -49 (6) | 402 (13) | 577 |

| Molecule <i>B</i> | <i>x</i> | <i>y</i> | <i>z</i> | U_{iso} |
|-------------------|----------|----------|-----------|------------------|
| H(2') | 739 (4) | 307 (3) | 964 (9) | 452 |
| H(3') | 862 (4) | 269 (3) | 909 (8) | 517 |
| H(4') | 899 (5) | 243 (4) | 601 (10) | 588 |
| H(5') | 782 (4) | 223 (4) | 417 (9) | 398 |
| H(6') | 654 (5) | 269 (3) | 467 (9) | 356 |
| H(9') | 541 (4) | 411 (3) | 1338 (9) | 569 |
| H(11') | 621 (5) | 525 (3) | 956 (10) | 492 |
| H(8' <i>a</i>) | 530 (5) | 306 (3) | 1305 (10) | 385 |
| H(8' <i>b</i>) | 486 (5) | 279 (3) | 1146 (10) | 382 |
| H(8' <i>c</i>) | 583 (6) | 266 (5) | 1151 (12) | 549 |
| H(10' <i>a</i>) | 608 (6) | 500 (4) | 1322 (11) | 588 |
| H(10' <i>b</i>) | 532 (7) | 558 (5) | 1206 (13) | 578 |
| H(10' <i>c</i>) | 518 (6) | 530 (5) | 1362 (14) | 592 |
| H(12' <i>a</i>) | 587 (7) | 448 (5) | 599 (14) | 583 |
| H(12' <i>b</i>) | 650 (7) | 491 (6) | 719 (15) | 568 |
| H(12' <i>c</i>) | 674 (6) | 419 (5) | 672 (13) | 598 |

gular dispositions of the C and O atoms attached to the S atom depart significantly from a regular tetrahedral arrangement with the usual large O(1)-S-O(2) and O(1')-S'-O(2') bond angles found in the sulphone group (117.3° av.) and small C(1)-S-C(7) and C(1')-S'-C(7') bond angles (106.1° av.). One of the S-C distances in each molecule is 0.04 Å larger than the other and this is further probable evidence of strain in the molecule.

Table 5. Displacements of atoms from the least-squares best planes (Å)

| Molecule <i>A</i> | From the plane through C(1), C(2)···C(6) | From the plane through C(7), C(8)···C(12) |
|-------------------|--|---|
| C(1) | 0.007 | C(7) 0.017 |
| C(2) | 0.005 | C(8) -0.020 |
| C(3) | -0.015 | C(9) 0.004 |
| C(4) | 0.012 | C(10) 0.015 |
| C(5) | 0.001 | C(11) -0.019 |
| C(6) | -0.010 | C(12) 0.003 |
| S | 0.164 | S' 0.152 |
| | | C(13) -0.064 |
| | | C(14) -0.010 |
| | | C(15) -0.048 |

| Molecule <i>B</i> | From the plane through C(1'), C(2')···C(6') | From the plane through C(7'), C(8')···C(12') |
|-------------------|---|--|
| C(1') | 0.010 | C(7') -0.019 |
| C(2') | -0.010 | C(8') 0.004 |
| C(3') | -0.001 | C(9') 0.020 |
| C(4') | 0.008 | C(10') -0.028 |
| C(5') | -0.009 | C(11') 0.012 |
| C(6') | 0.001 | C(12') 0.011 |
| S' | -0.144 | S' -0.147 |
| | | C(13') 0.050 |
| | | C(14') -0.207 |
| | | C(15') 0.037 |

The least-squares best planes passing through the six C atoms of each aromatic ring with deviations of atoms from these planes are given in Table 5. Despite the steric strain within the molecule the individual aromatic rings are approximately planar, but the S and some of the methyl C atoms, especially C(14'), are displaced considerable distances from the best planes. C(10')-C(14') is, however, significantly longer (1.572 Å) than the normal C-C length; the equivalent length (1.489 Å) of the other molecule is slightly shorter than the normal C-C length. This is probably due to a short contact. To relieve the strain, the two aromatic rings of both molecules are mutually inclined at angles of 87.18° and 86.91°.

In view of the foregoing evidence of extensive strain it is hardly surprising that the molecule is unstable.

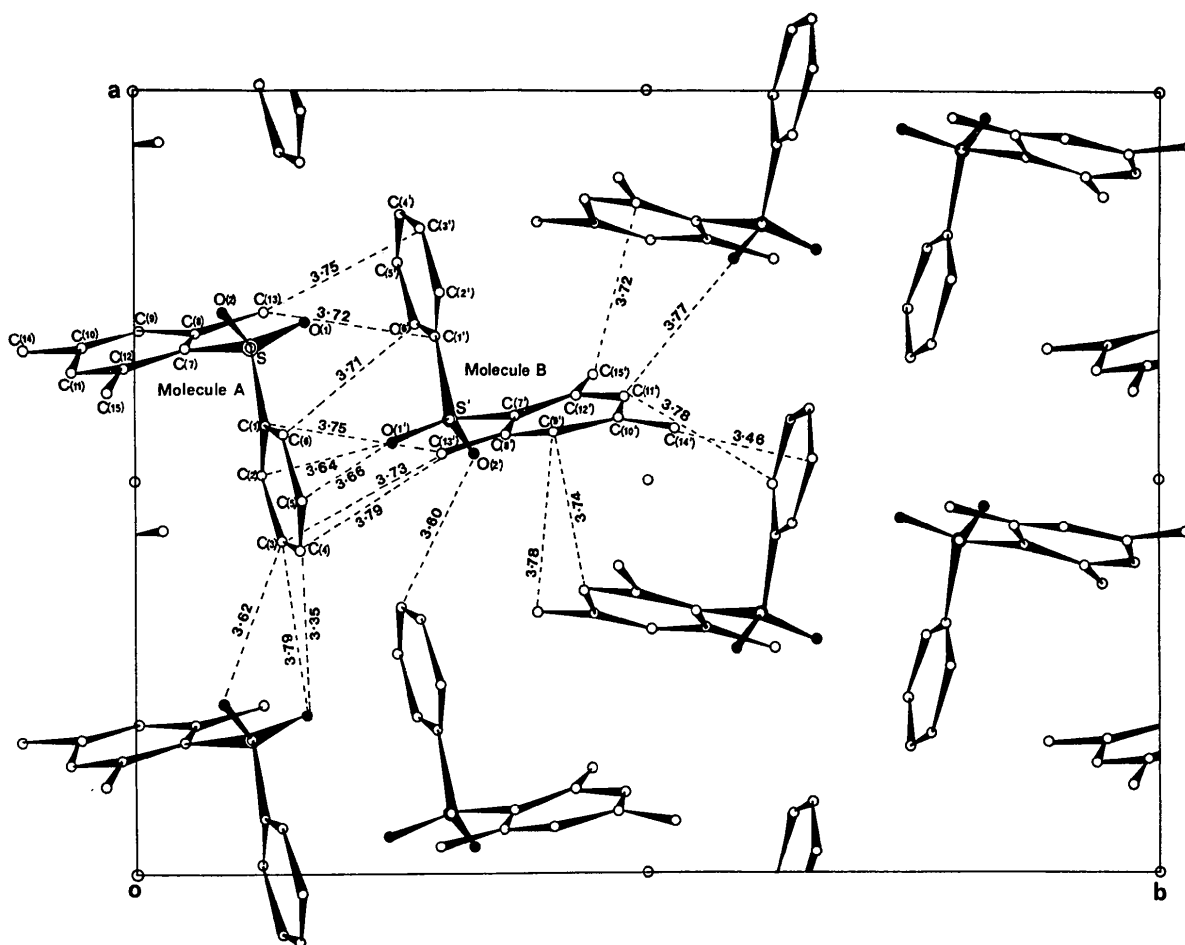


Fig. 2. The structure of phenyl mesityl sulphone viewed along [001], showing all intermolecular distances (excluding H atoms) of less than 3.8 Å.

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