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## Crystallographic Characterization of Reaction Intermediates with Bridgehead Double Bonds: Structures of Diels–Alder Adducts of (*E*)- and (*Z*)-9-Thiabicyclo[3.3.1]non-1-ene Derivatives with 1,3-Diphenylisobenzofuran

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### Abstract

Adduct *B*, (1*R*\*,2*R*\*,9*S*\*,10*S*\*,13*S*\*)-2,9-diphenyl-18-oxa-17-thiapentacyclo[11.3.1.1<sup>2,9</sup>.0<sup>1,10</sup>.0<sup>3,8</sup>]octadeca-3(8),4,6-triene 17,17-dioxide, C<sub>28</sub>H<sub>26</sub>O<sub>3</sub>S, *M<sub>r</sub>* = 442.58, monoclinic, *P*<sub>2</sub><sub>1</sub>/*n*, *a* = 16.186 (10), *b* = 9.452 (4), *c* = 15.583 (4) Å, β = 111.06 (4)°, *V* = 2225 (2) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.319 g cm<sup>-3</sup>, λ(Cu *Kα*) = 1.5418 Å, μ = 14.8 cm<sup>-1</sup>, *F*(000) = 936, *T* = 298 K, *R* = 0.047, *wR* = 0.044 for 2317 unique observed reflections with *I* > 2σ(*I*). Adduct *D*, (1*R*\*,2*R*\*,9*S*\*,10*R*\*,13*S*\*)-13-methyl-2,9-diphenyl-18-oxa-17-thiapentacyclo[11.3.1.1<sup>2,9</sup>.0<sup>1,10</sup>.0<sup>3,8</sup>]octadeca-3(8),4,6-triene 17,17-dioxide, C<sub>29</sub>H<sub>28</sub>O<sub>3</sub>S, *M<sub>r</sub>* = 456.61, monoclinic, *P*<sub>2</sub><sub>1</sub>/*n*, *a* = 11.343 (3), *b* = 19.323 (5), *c* = 11.006 (2) Å, β = 106.70 (2)°, *V* = 2311 (1) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.311 g cm<sup>-3</sup>, λ(Cu *Kα*) = 1.5418 Å, μ = 14.4 cm<sup>-1</sup>, *F*(000) = 968, *T* = 298 K, *R* = 0.041, *wR* = 0.044 for 2351 unique observed reflections with *I*

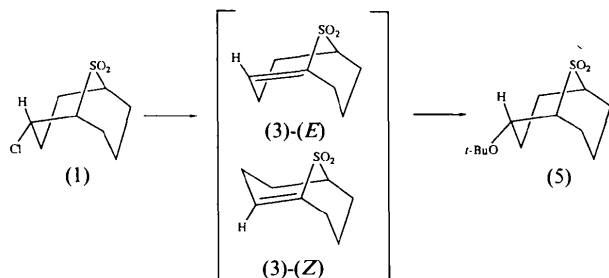
> 2σ(*I*). The Diels–Alder addition of a diene to 9-thiabicyclo[3.3.1]non-1-ene can take place in two ways, leaving the ring-junction hydrogen in the adduct in the *endo* or *exo* configuration. Also, the diene 1,3-diphenylisobenzofuran can add with its oxygen on the same (*syn*) side as the sulfur atom, or on the opposite (*anti*) side. Adduct *B* is shown to have the *exo*, *anti* configuration, while adduct *D*, a methyl derivative, has the *endo*, *anti* configuration. The crystals of adduct *B* contain a 15% admixture of adduct *C*, the *endo* isomer of *B*. Bond distances and angles reflect strain and overcrowding; short intramolecular non-bonded contacts are O(sulfone)⋯C(aromatic) = 2.869 (5) Å in adduct *D*, and H⋯H = 1.88 (6) Å between hydrogens on the terminal carbons of the chair–chair bicyclononane moiety of adduct *B*.

### Introduction

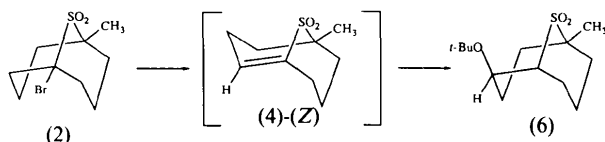
In a program (Wiseman and co-workers) aimed at exploring the stabilities of bicyclic molecules with a

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double bond to a bridgehead carbon atom, the reaction of (1) with potassium *t*-butoxide (Paquette & Houser, 1969) was considered:

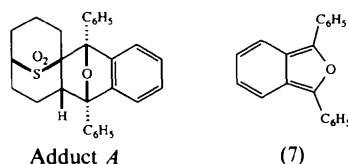


Of the two possible intermediates in this reaction, the *zusammen* isomer (3)-(Z) can be assumed to be the more stable one, as it lacks the twisted double bond (*trans* in the six-membered ring) of the *entgegen* isomer (3)-(E). The related reaction (Quinn, Wiseman & Calabrese, 1973), in the presence of potassium *t*-butoxide:



presents a similar question as to the *Z* or *E* configuration of the intermediate, here differing from (3) only in the presence of a methyl on the distal bridgehead carbon. The stereochemistry of (5) and (6) was established by NMR spectroscopy (Paquette & Houser, 1969; Quinn, Wiseman & Calabrese, 1973). The fact that (5) and (6) differ in configuration at the *t*-butoxy-substituted carbon led Quinn, Wiseman & Calabrese (1973) to conclude that the relevant isomer, *Z* or *E*, of the intermediate in the two reactions is not the same.

In order to explore the nature of the intermediate, the reaction (1)→(5) was carried out in the presence of 1,3-diphenylisobenzofuran, (7), which was expected to intercept the intermediate by formation of a Diels–Alder adduct. Two crystallizable products were formed, in nearly equal yield. These were designated as adducts *A* and *B*. The crystal structure of adduct *A* has been determined (Quinn, Wiseman & Calabrese, 1973) and its stereochemistry found to be as shown.



The hydrogen on the ring fusion in adduct *A* is *exo* (*syn* to the sulfone group), requiring the adjacent sulfone-containing ring to be chair, and thereby indicating that the relevant reaction intermediate is (3)-(E). There are four possible adduct isomers, represented by *exo* or *endo* hydrogen at the ring junction (from *E* or *Z* intermediates), and *syn* or *anti* furan oxygen disposition.

When the reaction (2)→(6) was carried out in the presence of 1,3-diphenylisobenzofuran, one crystalline adduct, designated *D*, was isolated. Adduct *D* was tentatively assigned an *endo* ring junction, by the reasoning based on the configuration of (5) and (6), and the *exo* junction of adduct *A*. This assignment is further strengthened by the following observations: 9-thiabicyclo[3.3.1]non-1-ene is a compound stable enough to be isolated, and it is therefore almost certainly in the less-strained (*Z*) form (8) (Quinn & Wiseman, 1973). Formation of its Diels–Alder adduct (9) and oxidation to a sulfone gives an isomer of adducts *A* and *B*, designated adduct *C* (Quinn, Wiseman & Calabrese, 1973). Methylation of adduct *C* at the bridgehead position gave a product identical to adduct *D*. These results prove that (9) and adducts *C* and *D* have the same ring junction, and strongly indicate that it is *endo*. Their furan oxygen orientation must be the same, but is not established whether it is *syn* or *anti*.

The crystallographic work was undertaken to confirm the *endo* orientation of the hydrogen at the ring junction in adducts *D* and *C*, and to determine their furan oxygen orientation. Another crystallographic objective was to resolve an ambiguity in the configuration of adduct *B*. The formation of *B* in equal amounts with the *exo*, *syn* adduct *A* suggested that *B* might be the *exo*, *anti* isomer, but the possibility that it was an *endo* isomer could not be ruled out on chemical grounds.

## Experimental

Colorless crystals of adduct *B* were grown from ethyl acetate/benzene solution and crystals of adduct *D* were grown from ethyl acetate/hexane. Specimens measuring 0.2 × 0.3 × 0.4 mm (adduct *B*) and 0.2 × 0.2 × 0.4 mm (adduct *D*) were used for data collection on a Syntex P1 diffractometer using a graphite monochromator. Cell parameters were determined from 15 reflections with 2θ in the 40 to 80° range. Diffracted intensities were measured in the θ:2θ scan mode with scan speeds of 1.5–24.0° min<sup>-1</sup> for adduct *B*, 2.0–24.0° min<sup>-1</sup> for adduct *D*. Data collected, for adduct *B*, to 2θ<sub>max</sub> = 120°, 0 ≤ h ≤ 15, 0 ≤ k ≤ 10, -17 ≤ l ≤ 15, 3361 unique reflections measured, of these 2325 had I > 2σ(I). Data for adduct *D* were collected to 2θ<sub>max</sub> = 110°, 0 ≤ h ≤ 12, 0 ≤ k ≤ 20, -10 ≤ l ≤ 10, 2864 unique reflections measured,

2378 had  $I > 2\sigma(I)$ . Three standard reflections showed no significant variation. No corrections were made for absorption.

The structure of adduct *B* was solved with direct methods using the programs *SIGMA2* and *TANGEN* of the *XRAY72* package (Stewart, Kundell & Baldwin, 1970). An *E* map of 376 phased reflections ( $E > 1.6$ ) showed all 32 non-hydrogen atoms. The structure was refined with the least-squares program *CLS* (Schilling, 1970), minimizing  $\sum w(|F_o| - k|F_c|)^2$ , with  $w = \sigma^2(F)$ , where  $\sigma(F) = \sigma(I)/(2F)$ . A  $\Delta F$  synthesis revealed the hydrogen atoms and one prominent peak, which could not be assigned as a hydrogen atom. Continued refinement with anisotropic thermal parameters for C, O and S, isotropic for H gave  $R = 0.065$ . A  $\Delta F$  synthesis showed the previously unaccounted for peak at (0.609, 0.414, 0.803). This peak, designated C(3*A*), was now interpreted as an alternative position for C(3). Since there is no conformational flexibility at C(3), this interpretation implies the presence of a chemically distinct molecule (adduct *C*) substituting for the molecules of adduct *B* in the crystal. In the subsequent refinement the occupancies of C(3) and C(3*A*) were adjusted, keeping their sum equal to unity. The values 0.85 and 0.15 were found to optimize the agreement. To correct for a downward trend in  $w(\Delta F)^2$  with  $|F|$  the least-squares weights were replaced by  $w = [\sigma^2(F) + KF_o^2]^{-1}$ , where  $\sigma(F)$  is based on counting statistics, and  $K = 0.0001$  was determined empirically to make  $w(\Delta F)^2$  approximately independent of  $|F|$ . With eight extinction-affected reflections deleted the refinement gave  $R = 0.047$  and  $wR = 0.044$ , for 2317 reflections. Maximum  $\Delta/\sigma = 0.7$  on the last cycle, for  $x$  of C(4),  $\Delta\rho_{\max} = 0.25$ ,  $\Delta\rho_{\min} = -0.25 \text{ e } \text{Å}^{-3}$ , both in the vicinity of the sulfur atom. The final parameters are listed in Table 1.\*

The structure of adduct *D* was solved with *MULTAN* (Germain, Main & Woolfson, 1971), an *E* map of 212 phased reflections ( $E > 1.8$ ) showing all 33 non-hydrogen atoms. Following refinement with *CLS* (Schilling, 1970), a  $\Delta F$  synthesis revealed all 28 hydrogen atoms. Least-squares weights  $w = [\sigma^2(F) + KF_o^2]^{-1}$  were employed, with  $K = 0.0001$  adjusted to make  $w(\Delta F)^2$  constant in  $|F|$ . Twenty-seven reflections, suffering from extinction effects or showing abnormal scan profiles, were omitted from the refinement. Final  $R = 0.041$ ,  $wR = 0.044$  for 2351 reflections. Maximum  $\Delta/\sigma = 0.6$ , for  $x$  of C(3), final  $\Delta\rho_{\max} = 0.18$ ,  $\Delta\rho_{\min} = -0.29 \text{ e } \text{Å}^{-3}$ , both near the sulfur atom. The final parameters are given in Table

\* Lists of anisotropic thermal parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52388 (33 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates and equivalent isotropic [isotropic for C(3*A*) and H] thermal parameters ( $\text{Å}^2$ ) for adduct *B*

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}/U$
C(1)	0.4559 (2)	0.2641 (3)	0.6865 (2)	0.0467 (8)
C(2)	0.5277 (2)	0.3049 (3)	0.7797 (2)	0.0662 (8)
C(3)†	0.5310 (2)	0.4531 (4)	0.8081 (8)	0.0672 (12)
C(3 <i>A</i> )†	0.5921 (11)	0.4219 (20)	0.7979 (13)	0.0469 (8)
C(4)	0.5508 (3)	0.5445 (3)	0.7348 (2)	0.0770 (10)
C(5)	0.4932 (2)	0.5180 (3)	0.6329 (2)	0.0713 (8)
C(6)	0.3967 (2)	0.5631 (3)	0.6045 (2)	0.0865 (11)
C(7)	0.3475 (2)	0.4862 (3)	0.6562 (2)	0.0749 (8)
C(8)	0.3613 (2)	0.3249 (3)	0.6629 (2)	0.0625 (8)
C(9)	0.4502 (2)	0.0974 (3)	0.7012 (2)	0.0500 (8)
C(10)	0.5411 (2)	0.0284 (3)	0.7258 (2)	0.0553 (8)
C(11)	0.5760 (2)	-0.0639 (3)	0.6788 (2)	0.0711 (8)
C(12)	0.6622 (2)	-0.1101 (3)	0.7240 (3)	0.0935 (11)
C(13)	0.7105 (2)	-0.0676 (4)	0.8104 (3)	0.0982 (11)
C(14)	0.6762 (2)	0.0257 (4)	0.8589 (2)	0.0822 (8)
C(15)	0.5890 (2)	0.0711 (3)	0.8148 (2)	0.0615 (8)
C(16)	0.5289 (2)	0.1735 (3)	0.8401 (2)	0.0515 (8)
C(17)	0.3737 (2)	0.0171 (3)	0.6357 (2)	0.0530 (8)
C(18)	0.3657 (2)	0.0006 (4)	0.5447 (2)	0.0691 (8)
C(19)	0.2976 (2)	-0.0772 (4)	0.4844 (2)	0.0798 (11)
C(20)	0.2366 (2)	-0.1401 (4)	0.5148 (2)	0.0818 (10)
C(21)	0.2435 (2)	-0.1251 (3)	0.6043 (2)	0.0800 (11)
C(22)	0.3119 (2)	-0.0471 (3)	0.6659 (2)	0.0630 (8)
C(23)	0.5410 (2)	0.1980 (3)	0.9390 (2)	0.0536 (8)
C(24)	0.4749 (2)	0.1662 (3)	0.9721 (2)	0.0559 (8)
C(25)	0.4877 (2)	0.1887 (3)	1.0640 (2)	0.0684 (8)
C(26)	0.5656 (2)	0.2423 (4)	1.1230 (2)	0.0737 (8)
C(27)	0.6311 (2)	0.2762 (4)	1.0910 (2)	0.0797 (10)
C(28)	0.6195 (2)	0.2559 (4)	0.9991 (2)	0.0767 (10)
S(29)	0.4954 (1)	0.3348 (1)	0.6020 (1)	0.0653 (2)
O(30)	0.4438 (1)	0.1069 (2)	0.7911 (1)	0.0476 (6)
O(31)	0.4301 (2)	0.3137 (2)	0.5108 (1)	0.0876 (7)
O(32)	0.5850 (1)	0.2911 (2)	0.6179 (2)	0.0934 (8)
H(2)	0.596 (2)	0.322 (4)	0.761 (2)	0.140 (13)
H(3 <i>A</i> )	0.588 (2)	0.465 (3)	0.866 (2)	0.084 (9)
H(3 <i>B</i> )	0.465 (2)	0.455 (3)	0.808 (2)	0.105 (11)
H(4 <i>A</i> )	0.618 (2)	0.544 (4)	0.740 (2)	0.136 (13)
H(4 <i>B</i> )	0.540 (2)	0.629 (3)	0.747 (2)	0.066 (8)
H(5)	0.523 (2)	0.570 (3)	0.594 (2)	0.091 (10)
H(6 <i>A</i> )	0.399 (2)	0.660 (3)	0.619 (2)	0.086 (9)
H(6 <i>B</i> )	0.369 (2)	0.537 (3)	0.534 (2)	0.110 (11)
H(7 <i>A</i> )	0.280 (2)	0.503 (3)	0.625 (2)	0.081 (9)
H(7 <i>B</i> )	0.361 (2)	0.524 (3)	0.719 (2)	0.067 (9)
H(8 <i>A</i> )	0.328 (1)	0.275 (2)	0.598 (1)	0.054 (8)
H(8 <i>B</i> )	0.343 (2)	0.287 (3)	0.712 (2)	0.085 (10)
H(11)	0.542 (2)	-0.096 (3)	0.612 (2)	0.081 (9)
H(12)	0.688 (2)	-0.177 (3)	0.691 (2)	0.092 (10)
H(13)	0.774 (2)	-0.105 (3)	0.839 (2)	0.115 (11)
H(14)	0.710 (2)	0.068 (3)	0.921 (2)	0.094 (10)
H(18)	0.408 (2)	0.044 (3)	0.523 (2)	0.063 (8)
H(19)	0.294 (2)	-0.084 (3)	0.423 (2)	0.094 (10)
H(20)	0.189 (2)	-0.188 (3)	0.473 (2)	0.104 (10)
H(21)	0.198 (2)	-0.163 (3)	0.625 (2)	0.101 (10)
H(22)	0.318 (2)	-0.034 (3)	0.727 (2)	0.081 (9)
H(24)	0.419 (2)	0.127 (3)	0.929 (2)	0.062 (8)
H(25)	0.443 (2)	0.161 (3)	1.088 (2)	0.080 (9)
H(26)	0.574 (2)	0.258 (3)	1.194 (2)	0.086 (10)
H(27)	0.683 (2)	0.318 (3)	1.131 (2)	0.095 (10)
H(28)	0.667 (2)	0.281 (3)	0.977 (2)	0.096 (10)

† C(3) and C(3*A*) represent alternative positions of the same atom with occupancies 0.85 and 0.15, respectively.

2.\* All structure-factor calculations used atomic scattering factors for C, O and S from *International Tables for X-ray Crystallography* (1962), and for H from Stewart, Davidson & Simpson (1965).

## Discussion

Selected bond distances and angles, and torsion angles are listed in Table 3. The atom numbering is

\* See deposition footnote.

Table 2. Fractional atomic coordinates and equivalent isotropic (isotropic for H) thermal parameters (Å<sup>2</sup>) for adduct D
$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U <sub>eq</sub> /U
C(1)	0.1914 (2)	0.1053 (1)	0.0966 (2)	0.0333 (7)
C(2)	0.0724 (2)	0.1382 (1)	0.1187 (3)	0.0381 (7)
C(3)	0.0741 (3)	0.2167 (1)	0.1365 (3)	0.0497 (8)
C(4)	0.1161 (3)	0.2583 (2)	0.0380 (3)	0.0551 (8)
C(5)	0.2333 (3)	0.2337 (2)	0.0050 (3)	0.0468 (8)
C(6)	0.2051 (3)	0.1986 (2)	-0.1257 (3)	0.0571 (8)
C(7)	0.1204 (3)	0.1355 (2)	-0.1416 (3)	0.0562 (8)
C(8)	0.1674 (2)	0.0794 (1)	-0.0415 (3)	0.0431 (8)
C(9)	0.2184 (2)	0.0428 (1)	0.1962 (2)	0.0346 (7)
C(10)	0.2626 (2)	0.0741 (1)	0.3291 (2)	0.0361 (8)
C(11)	0.3761 (2)	0.0735 (2)	0.4199 (3)	0.0449 (8)
C(12)	0.3851 (3)	0.1097 (2)	0.5319 (3)	0.0529 (8)
C(13)	0.2865 (3)	0.1453 (2)	0.5501 (3)	0.0580 (8)
C(14)	0.1720 (3)	0.1444 (2)	0.4582 (3)	0.0498 (8)
C(15)	0.1621 (2)	0.1072 (1)	0.3487 (2)	0.0380 (8)
C(16)	0.0557 (2)	0.0936 (1)	0.2305 (3)	0.0383 (8)
C(17)	0.2824 (2)	-0.0208 (1)	0.1698 (2)	0.0371 (8)
C(18)	0.3963 (3)	-0.0713 (2)	0.1458 (3)	0.0471 (8)
C(19)	0.4554 (3)	-0.0770 (2)	0.1256 (3)	0.0545 (8)
C(20)	0.4027 (3)	-0.1406 (2)	0.1303 (3)	0.0570 (8)
C(21)	0.2912 (3)	-0.1446 (2)	0.1541 (3)	0.0584 (8)
C(22)	0.2307 (3)	-0.0851 (2)	0.1755 (3)	0.0466 (8)
C(23)	-0.0701 (2)	0.0861 (2)	0.2493 (3)	0.0437 (8)
C(24)	-0.1721 (3)	0.1217 (2)	0.1793 (3)	0.0616 (10)
C(25)	-0.2859 (3)	0.1110 (2)	0.1996 (3)	0.0746 (12)
C(26)	-0.2970 (3)	0.0648 (2)	0.2904 (3)	0.0807 (10)
C(27)	-0.1960 (3)	0.0291 (2)	0.3610 (4)	0.0752 (10)
C(28)	-0.0826 (3)	0.0394 (2)	0.3404 (3)	0.0595 (8)
C(33)	0.3261 (3)	0.2927 (2)	0.0140 (3)	0.0679 (8)
S(29)	0.3118 (1)	0.17059 (4)	0.1207 (1)	0.0360 (12)
O(30)	0.0925 (2)	0.0264 (1)	0.1919 (2)	0.0379 (6)
O(31)	0.4134 (2)	0.1427 (1)	0.0818 (2)	0.0528 (6)
O(32)	0.3409 (2)	0.2021 (1)	0.2451 (2)	0.0479 (6)
H(2)	0.004 (2)	0.125 (1)	0.047 (2)	0.037 (6)
H(3A)	-0.017 (2)	0.232 (1)	0.132 (2)	0.060 (9)
H(3B)	0.120 (2)	0.228 (1)	0.218 (2)	0.046 (8)
H(4A)	0.049 (2)	0.257 (1)	-0.038 (2)	0.066 (9)
H(4B)	0.131 (2)	0.308 (1)	0.066 (3)	0.076 (10)
H(6A)	0.166 (2)	0.235 (1)	-0.187 (3)	0.071 (9)
H(6B)	0.291 (2)	0.185 (1)	-0.137 (2)	0.065 (9)
H(7A)	0.042 (2)	0.151 (1)	-0.137 (2)	0.046 (8)
H(7B)	0.113 (3)	0.114 (2)	-0.229 (3)	0.081 (10)
H(8A)	0.101 (2)	0.043 (1)	-0.052 (2)	0.047 (8)
H(8B)	0.247 (2)	0.060 (2)	-0.051 (2)	0.042 (8)
H(11)	0.450 (2)	0.052 (1)	0.403 (3)	0.066 (9)
H(12)	0.459 (3)	0.110 (1)	0.595 (3)	0.079 (10)
H(13)	0.301 (3)	0.171 (1)	0.633 (3)	0.070 (9)
H(14)	0.098 (2)	0.167 (1)	0.474 (3)	0.063 (9)
H(18)	0.435 (2)	0.028 (1)	0.140 (2)	0.052 (8)
H(19)	0.534 (3)	-0.074 (2)	0.107 (3)	0.090 (11)
H(20)	0.443 (2)	-0.182 (1)	0.114 (2)	0.066 (9)
H(21)	0.253 (3)	-0.187 (1)	0.157 (3)	0.068 (9)
H(22)	0.150 (3)	-0.086 (1)	0.194 (3)	0.062 (9)
H(24)	-0.164 (3)	0.151 (1)	0.117 (3)	0.072 (9)
H(25)	-0.357 (3)	0.136 (2)	0.152 (3)	0.103 (11)
H(26)	-0.378 (3)	0.057 (2)	0.310 (3)	0.100 (11)
H(27)	-0.203 (3)	-0.001 (2)	0.428 (3)	0.108 (11)
H(28)	-0.009 (3)	0.017 (2)	0.395 (3)	0.089 (10)
H(33A)	0.287 (3)	0.327 (2)	-0.044 (3)	0.091 (10)
H(33B)	0.412 (3)	0.275 (2)	-0.004 (3)	0.111 (13)
H(33C)	0.344 (3)	0.313 (2)	0.091 (3)	0.081 (10)

given in Fig. 1. Figs. 2 and 3 show ORTEP (Johnson, 1965) stereoviews of the molecules of adducts B and D, respectively. These show that adduct B has the *exo, anti* and adduct D the *endo, anti* configuration. In the *exo* configuration, at C(2), the ring consisting of S and C(1) to C(5) assumes a chair conformation (Fig. 2), in the *endo* configuration the ring is in a boat conformation, (Fig. 3). The alternative site [C(3A)] of C(3) corresponds to the boat conformation for this ring. Thus the 15% admixture in the crystals of adduct B is the *endo, anti* isomer of

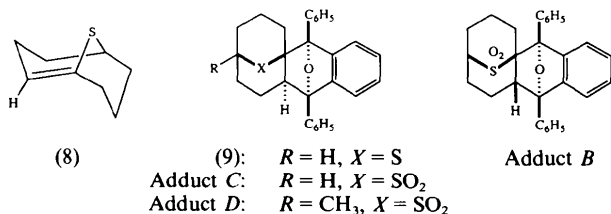
Table 3. Selected bond lengths (Å), bond angles (°) and torsion angles (°)

	Adduct B	Adduct D
C(1)—C(2)	1.548 (4)	1.573 (4)
C(1)—C(8)	1.550 (4)	1.548 (4)
C(1)—C(9)	1.599 (4)	1.600 (4)
C(1)—S(29)	1.788 (3)	1.822 (3)
C(2)—C(3)	1.464 (5)	1.529 (4)
C(2)—C(3A)	1.476 (19)	
C(2)—C(16)	1.554 (4)	1.558 (4)
C(3)—C(4)	1.555 (6)	1.531 (5)
C(3A)—C(4)	1.512 (18)	
C(4)—C(5)	1.546 (4)	1.550 (5)
C(5)—C(6)	1.523 (5)	1.539 (4)
C(5)—C(33)		1.535 (4)
C(5)—S(29)	1.801 (3)	1.803 (3)
C(6)—C(7)	1.508 (6)	1.531 (5)
C(7)—C(8)	1.539 (5)	1.528 (4)
C(9)—C(10)	1.527 (4)	1.528 (4)
C(9)—O(30)	1.444 (4)	1.450 (3)
C(10)—C(11)	1.383 (5)	1.385 (3)
C(10)—C(15)	1.384 (4)	1.377 (4)
C(15)—C(16)	1.522 (5)	1.522 (3)
C(16)—C(23)	1.500 (4)	1.507 (4)
C(16)—O(30)	1.456 (3)	1.464 (3)
S(29)—O(31)	1.448 (2)	1.444 (2)
S(29)—O(32)	1.441 (3)	1.447 (2)
C(2)—C(1)—C(8)	118.3 (3)	111.5 (2)
C(2)—C(1)—C(9)	100.0 (2)	101.7 (2)
C(2)—C(1)—S(29)	104.5 (2)	109.8 (2)
C(8)—C(1)—C(9)	107.3 (2)	111.9 (2)
C(8)—C(1)—S(29)	105.8 (2)	106.3 (2)
C(9)—C(1)—S(29)	121.9 (2)	115.8 (2)
C(1)—C(2)—C(3)	117.1 (2)	116.2 (2)
C(1)—C(2)—C(3A)	127.5 (7)	
C(1)—C(2)—C(16)	102.1 (2)	101.7 (2)
C(3)—C(2)—C(16)	126.1 (3)	116.6 (2)
C(3A)—C(2)—C(16)	128.9 (7)	
C(2)—C(3)—C(4)	107.7 (3)	115.2 (3)
C(2)—C(3A)—C(4)	109.4 (10)	
C(3)—C(4)—C(5)	117.2 (3)	117.9 (2)
C(3A)—C(4)—C(5)	120.5 (7)	
C(4)—C(5)—C(6)	115.5 (3)	113.1 (2)
C(4)—C(5)—S(29)	111.6 (2)	109.0 (2)
C(4)—C(5)—C(33)		112.1 (3)
C(6)—C(5)—C(33)		110.0 (3)
C(6)—C(5)—S(29)	107.9 (2)	106.9 (2)
C(33)—C(5)—S(29)		105.5 (2)
C(5)—C(6)—C(7)	113.1 (3)	114.4 (3)
C(6)—C(7)—C(8)	115.0 (3)	113.9 (2)
C(1)—C(8)—C(7)	119.4 (3)	113.9 (2)
C(1)—C(9)—C(10)	110.9 (2)	107.6 (2)
C(1)—C(9)—C(17)	118.5 (2)	119.6 (2)
C(1)—C(9)—O(30)	96.0 (2)	98.6 (2)
C(10)—C(9)—C(17)	116.2 (2)	117.8 (2)
C(10)—C(9)—O(30)	100.5 (2)	99.6 (2)
C(17)—C(9)—O(30)	111.3 (2)	110.0 (2)
C(9)—C(10)—C(15)	105.7 (3)	106.0 (2)
C(11)—C(10)—C(15)	121.7 (3)	122.1 (2)
C(10)—C(15)—C(16)	105.3 (2)	105.9 (2)
C(2)—C(16)—C(15)	102.8 (3)	109.5 (2)
C(2)—C(16)—C(23)	117.9 (2)	119.8 (2)
C(2)—C(16)—O(30)	103.0 (2)	98.7 (2)
C(15)—C(16)—C(23)	120.3 (2)	116.7 (2)
C(15)—C(16)—O(30)	99.3 (2)	100.3 (2)
C(23)—C(16)—O(30)	110.8 (2)	108.4 (2)
C(9)—C(17)—C(18)	120.3 (3)	121.7 (2)
C(9)—C(17)—C(22)	120.7 (3)	119.5 (3)
C(16)—C(23)—C(24)	121.2 (2)	123.5 (3)
C(16)—C(23)—C(28)	120.2 (3)	117.4 (2)
C(1)—S(29)—C(5)	96.7 (2)	99.7 (1)
C(1)—S(29)—O(31)	111.8 (1)	109.1 (1)
C(1)—S(29)—O(32)	110.0 (1)	112.8 (1)
C(5)—S(29)—O(31)	110.2 (2)	108.5 (1)
C(5)—S(29)—O(32)	108.5 (1)	108.4 (1)
O(31)—S(29)—O(32)	117.6 (2)	116.9 (1)
C(9)—O(30)—C(16)	98.7 (2)	99.0 (2)
C(8)—C(1)—C(2)—C(3)	-43.0 (4)	-109.4 (3)
C(8)—C(1)—C(2)—C(3A)	-94.0 (8)	
C(8)—C(1)—C(2)—C(16)	99.1 (4)	122.9 (3)
C(9)—C(1)—C(2)—C(3)	-158.9 (3)	131.2 (3)
C(9)—C(1)—C(2)—C(3A)	150.1 (8)	
C(9)—C(1)—C(2)—C(16)	-16.8 (3)	3.5 (3)
S(29)—C(1)—C(2)—C(3)	74.3 (3)	8.0 (3)
S(29)—C(1)—C(2)—C(3A)	23.3 (8)	
S(29)—C(1)—C(2)—C(16)	-143.6 (3)	-119.6 (3)

Table 3 (cont.)

	Adduct B	Adduct D
C(2)—C(1)—C(8)—C(7)	60.8 (4)	57.2 (3)
S(29)—C(1)—C(8)—C(7)	-55.8 (4)	-62.3 (3)
C(2)—C(1)—C(9)—C(10)	-55.4 (3)	-70.6 (3)
C(2)—C(1)—C(9)—C(17)	166.4 (3)	151.3 (3)
C(2)—C(1)—C(9)—O(30)	48.2 (3)	32.4 (3)
C(1)—C(2)—C(16)—C(15)	83.1 (4)	66.3 (3)
C(1)—C(2)—C(16)—O(30)	-19.7 (3)	-37.9 (3)
C(9)—C(10)—C(15)—C(16)	-4.0 (4)	2.3 (3)

adduct *B*, previously designated adduct *C*. Adduct *C* has the same configuration as adduct *D*, differing from the latter in that it lacks the methyl group C(33).



The *endo* configuration of adduct *D* confirms the *Z* configuration of the intermediate alkene (4) formed by elimination of hydrogen bromide from the bromosulfone (2). This assignment is reasonable, since the proposed *syn E2* elimination should produce the more-stable *Z* isomer, rather than the *E* isomer, which would have a *trans* carbon double bond in a six-membered ring. It is noteworthy that both the intermediate alkene (4) and alkene (8) react stereoselectively with 1,3-diphenylisobenzofuran (7), in the sense that only the *anti* isomer is formed. This is in accord with Alder's *endo* rule for the Diels-Alder reaction (Alder & Stein, 1937). The bridging sulfur and sulfur dioxide groups function as activating substituents on the dienophilic carbon double bond. The preferred transition state for the cycloaddition places the sulfur atom in an *endo* relationship with respect to the diene (furan ring). This produces adducts with the *anti* relationship between sulfur and oxygen.

In contrast, no selectivity is evident in the reaction of (3)-(*E*) with 1,3-diphenylisobenzofuran; the *syn* adduct *A* and the *anti* adduct *B* are formed in approximately equal amounts. This lack of selectivity is a consequence of the greater strain and higher reactivity of (3)-(*E*) in relation to the (4)-(*Z*) intermediate in the (2)→(6) reaction.

The finding that the crystals of adduct *B* contain 15% adduct *C* must be ascribed to cycloaddition of 1,3-diphenylisobenzofuran with the *zusammen* isomer (3)-(*Z*). The origin of (3)-(*Z*) cannot be identified with certainty. It may be formed directly from chlorosulfone (1) in the reaction with potassium *t*-butoxide, or it may arise from isomerization of the more-strained stereoisomer (3)-(*E*).

The molecules of adducts *B* and *D* have regions of severe strain, as can be seen by inspecting the molecular parameters in Table 3. The junction of the 1,3-diphenylisobenzofuran moiety to the thiabicyclononane in the *exo* configuration (adduct *B*) produces a twist in the central part of the former as shown by the value  $-16.8 (3)^\circ$  of the C(9)—C(1)—C(2)—C(16) torsion angle, giving the bridged ring formed by carbon atoms 1—2—16—15—10—9 a 'twist boat' conformation. This strain also causes the  $74.3 (3)^\circ$  torsion angle S(29)—C(1)—C(2)—C(3) to depart from its expected value of  $60^\circ$  in the nominally rigid chair-chair thiabicyclononane moiety. By contrast, the *endo* juncture (adduct *D*) is less strained. The C(9)—C(1)—C(2)—C(16) torsion angle of  $3.5 (3)^\circ$  indicates a nearly ideal boat conformation for ring

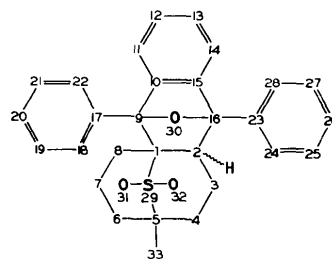


Fig. 1. Atom-numbering scheme for adducts *B* and *D*. C(33) is present only in adduct *D*.

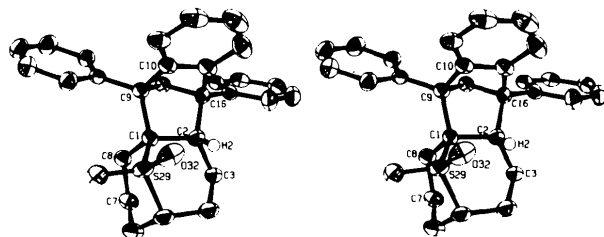


Fig. 2. Stereoview of adduct *B*. Atoms relevant to the discussion in the text are identified. The thermal-vibration ellipsoids are at 30% probability. Hydrogen atoms deleted, except H(2), which is shown as a sphere of arbitrary radius.

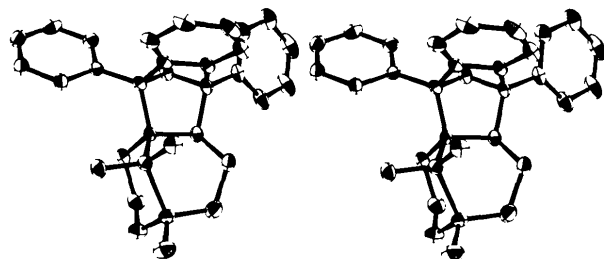


Fig. 3. Stereoview of adduct *D*, with thermal ellipsoids at 30% probability. The hydrogen atoms have been deleted.

1—2—16—15—10—9, and the 8.0 (3)° torsion angle S(29)—C(1)—C(2)—C(3) shows relatively little departure from an ideal boat in the chair–boat conformation of the thiabicyclononane moiety.

The difference in geometry about the C(1)—C(2) bond affects the positioning of the rigid benzo group relative to O(32) of the sulfone. In adduct *D* the benzo group is tilted toward the sulfone, producing an intramolecular contact of 2.869 (4) Å between O(32) and C(10), appreciably less than the van der Waals radius sum of 3.10 Å (Pauling, 1960). In adduct *B* this nonbonded contact is 3.218 (4) Å.

McCabe & Sim (1981, 1982) have studied the geometry of the 9-thiabicyclo[3.3.1]nonane 9,9-dioxide system in the 2,6-dichloro and 2,6-dinitrato derivatives. Despite the resulting close contact between C(3) and C(7), and their hydrogens, both compounds assume chair–chair conformations, as does the 9-thiabicyclo[3.3.1]nonane moiety in adduct *B*. In adduct *B* we find C(3)⋯C(7) = 3.077 (5) and H(3*B*)⋯H(7*B*) = 1.88 (6) Å. These distances are even shorter than the values 3.120 (4) and 3.128 (2) Å found for C(3)⋯C(7) in the 2,6-dichloro and 2,6-dinitrato derivatives, and 2.071 (28) Å for the corresponding H⋯H distance in 2,6-dinitrato derivative. As McCabe & Sim (1982) point out, these X-ray values for the H⋯H distance may understate the

closeness of approach, as the true internuclear C—H distances tend to be longer than the X-ray values.

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## Electron Density Distribution in a Bicyclo[1.1.0]butane

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#### Abstract

The difference electron densities in the bicyclo[1.1.0]butane derivative 4-phenyl-2,4,6-triazapentacyclo[5.4.2.0<sup>2.6</sup>.0<sup>8.10</sup>.0<sup>9.11</sup>]tridec-12-en-3,5-dione (I) have been determined experimentally at 98 (1) K from X-ray (Mo *K*α, λ = 0.71069 Å) diffraction data measured to (sinθ/λ)<sub>max</sub> = 1.15 Å<sup>-1</sup>. Crystal data: C<sub>16</sub>H<sub>13</sub>N<sub>3</sub>O<sub>2</sub>, *M<sub>r</sub>* = 279.3, orthorhombic, *Pbca*, *a* = 11.340 (1), *b* = 15.037 (1), *c* = 15.405 (1) Å, *V* =

2626.9 (6) Å<sup>3</sup>, *Z* = 8, *D<sub>x</sub>* = 1.38 Mg m<sup>-3</sup>, μ = 0.0901 mm<sup>-1</sup>, *F*(000) = 1168, final *R* = 0.052 for 3605 reflections. Based on the degree of inversion from tetrahedral geometry of the bridgehead C atoms in polycyclic systems, compound (I) lies on the transition from open bicyclo[1.1.0]butanes to propellanes. The very weak difference density contribution in the central C(1)—C(3) bond fits into the graduation along this line. The bonding maxima in the bicyclo[1.1.0]butane moiety and, to a lesser

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