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Key indicators

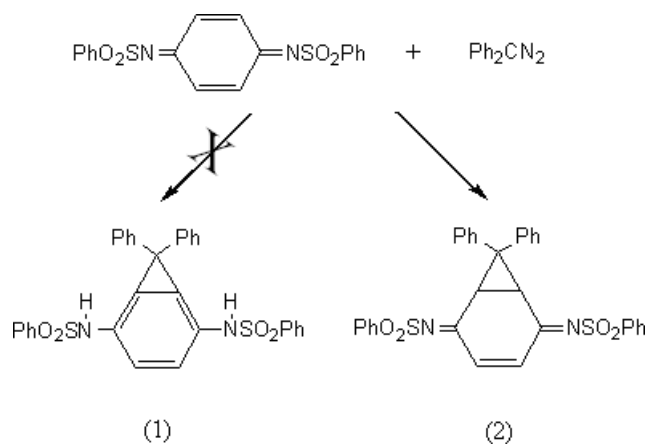
Single-crystal X-ray study
 $T = 110\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.002\text{ \AA}$
 R factor = 0.032
 wR factor = 0.087
Data-to-parameter ratio = 15.2For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.*N,N*-[(*Z,Z*)-7,7-Diphenylbicyclo[4.1.0]hept-3-ene-2,5-diylidene]dibenzenesulfonamide

The crystal structure of the addition product of *p*-quinone-benzenesulfonimide and diphenyldiazomethane, $\text{C}_{31}\text{H}_{24}\text{N}_2\text{O}_4\text{S}_2$, confirms earlier spectroscopic evidence that it is not a substituted benzocyclopropene, as previously claimed, but contains instead a bicyclic three-membered ring fused to a six-membered ring incorporating only one double bond.

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Comment

The title compound was reported (Mustafa & Kamel, 1953) to form a substituted benzocyclopropene, (1), which would have been possibly the earliest synthesis (Anet & Anet, 1964; Vogel *et al.*, 1965) of this type of unique structure. On the basis mainly of spectroscopic evidence (Pinkus & Tsuji, 1974; Jones *et al.*, 1974), the product was instead suggested to be a bicyclic structure, (2), of a three-membered ring fused to a six-membered one [Halton, 1973; since this review was published before the papers by Pinkus & Tsuji (1974) and Jones *et al.* (1974) appeared, these two references, which deal with the correction of the report by Mustafa & Kamel (1953), do not appear in the review; the numbering of the bicyclic compound without substituents is given in the Halton reference] [named by *Chem. Abstr.* (1974) as a bicyclo[4.1.0]hept-3-ene and by *Beilsteins Handbuch der Organischen Chemie* (1992) as *N,N'*-[(*Z,Z*)-7,7-diphenyl-bicyclo[4.1.0]hept-3-en-2,5-diylidene]-bis-benzolsulfonamid] incorporating only one double bond. The conclusive evidence for structure (2) is presented here. Structural features of (2) are displayed in Fig. 1.



Crystallographic data reveal several features worth noting, beginning with the observation that the central six-membered ring in question is not aromatic. The C5–C6 bond shows only

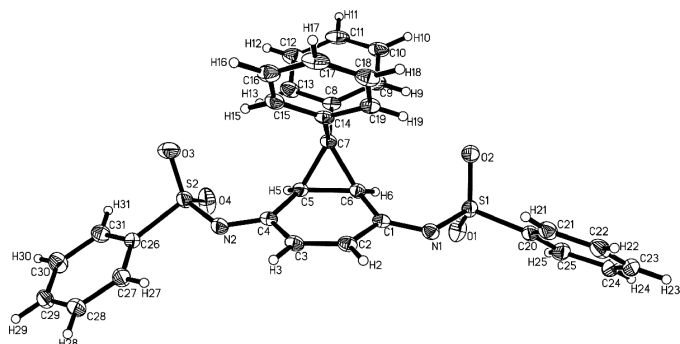


Figure 1

A view of the molecular structure of (2); displacement ellipsoids are drawn at the 50% probability level.

a slight decrease from an idealized single bond length [1.528 (2) Å]. The other two C—C bonds of the three-membered ring show comparable lengths of 1.532 (2) and 1.528 (2) Å for C6—C7 and C5—C7, respectively. The C2=C3 double bond distance is normal [1.340 (2) Å], while on either side the C1—C2 and C3—C4 ‘single’ bonds show contractions, with distances of 1.465 (2) and 1.464 (2) Å, indicative of at least some degree of resonance in the ring. The C1—C6 and C4—C5 bonds also show considerable contraction [1.483 (2) and 1.484 (2) Å], but are slightly closer to standard. Both C—N bonds are directed slightly below the plane of the ring as a result of the combination of the upper phenyl steric interaction with the twisting of the hexagon by the two four-coordinate C atoms. Both —SO₂Ph groups are directed towards the face of the central ring that is opposite to that containing the cyclopropane-bound phenyl groups; this configuration is again attributed to steric interactions. These substituents adopt different conformations in the solid state, breaking the potential mirror plane bisecting the molecule. This arrangement differs from that suggested in the original report (Pinkus & Tsuji, 1974), which was based solely on NMR data. It is also possible that the intramolecular hydrogen bonding between the cyclopropyl ring H atoms and the SO₂ O atoms has the effect of stabilizing this solid-state conformation. In solution, this asymmetric character is lost by free rotation around the N—S bonds, making the two outstretched phenyl groups indistinguishable by NMR. The internal angles of the cyclopropane ring are nearly ideally trigonal [59.91 (8), 60.19 (9) and 59.90 (9)°], while the two phenyl rings of C14 and C8 show the effects of the opposing side’s constriction, with an exaggerated 113.64 (11)° angle. All other bond lengths and angles fall within expected ranges. Selected geometric parameters are presented in Table 1 and intramolecular hydrogen-bond distances are presented in Table 2.

Experimental

Compound (2) was synthesized as described previously (Pinkus & Tsuji, 1974). Suitable diffraction-quality crystals were obtained by dissolving (2) in hot benzene, adding petroleum ether and allowing the mixture to stand [m.p. 475–476 K; literature (Mustafa & Kamel, 1953) 475 K].

Crystal data

C₃₁H₂₄N₂O₄S₂
M_r = 552.64
 Monoclinic, *P*2₁/*n*
a = 7.0546 (3) Å
b = 23.3933 (11) Å
c = 16.2515 (9) Å
 β = 102.405 (3)°
V = 2619.4 (2) Å³
Z = 4

D_x = 1.401 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 6775 reflections
 θ = 2.7–30.2°
 μ = 0.25 mm⁻¹
T = 110 (2) K
 Block, colorless
 0.26 × 0.22 × 0.15 mm

Data collection

Bruker X8 APEX CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan; (SADABS; Sheldrick, 1996)
 T_{\min} = 0.900, T_{\max} = 0.964
 53 078 measured reflections

5352 independent reflections
 4696 reflections with *I* > 2σ(*I*)
 R_{int} = 0.045
 θ_{max} = 26.4°
 h = -8 → 8
 k = -29 → 29
 l = -20 → 20

Refinement

Refinement on *F*²
 $R[F^2 > 2\sigma(F^2)]$ = 0.032
 $wR(F^2)$ = 0.087
 S = 1.03
 5352 reflections
 352 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.041P)^2 + 1.5285P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}}$ = 0.001
 $\Delta\rho_{\text{max}}$ = 0.34 e Å⁻³
 $\Delta\rho_{\text{min}}$ = -0.43 e Å⁻³

Table 1

Selected geometric parameters (Å, °).

C1—C2	1.4645 (19)	C4—C5	1.4835 (18)
C1—C6	1.4827 (19)	C5—C6	1.5278 (19)
C2—C3	1.340 (2)	C5—C7	1.5281 (18)
C3—C4	1.4635 (19)	C6—C7	1.5323 (18)
C6—C5—C7	60.19 (9)	C14—C7—C8	113.64 (11)
C5—C6—C7	59.91 (8)	C5—C7—C6	59.90 (9)

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C5—H5...O4	0.98	2.33	3.004 (2)	125
C6—H6...O1	0.98	2.49	3.148 (2)	124

H atoms were included in calculated positions (C—H = 0.930 Å) and treated as riding; isotropic displacement parameters were fixed [$U_{\text{iso}}(\text{H}) = 1.2U_{\text{iso}}(\text{C})$].

Data collection: APEX2 (Bruker, 2003); cell refinement: APEX2; data reduction: SAINT-Plus (Bruker, 2003); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Sheldrick, 2000); software used to prepare material for publication: SHELXTL.

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