Influence of Benzo-bridging on the Stability of 6aλ^4-Thia-1,2,5,6-tetraazapentalenic Systems

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Methylation of the phenylhydrazone derived from 8-oxo-8*H*-indeno[1,2-*d*]-1,2,3-thiadiazole **5** with Meerwein's reagent furnishes the two methylated products **7** and **8**. Single crystal X-ray analyses of these compounds reveal no significant S...NPh interaction, thus excluding a thiapentalene structure.

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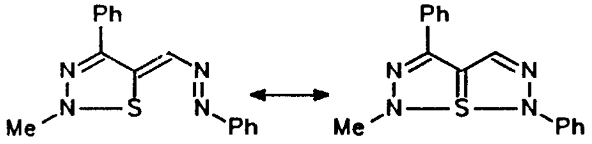
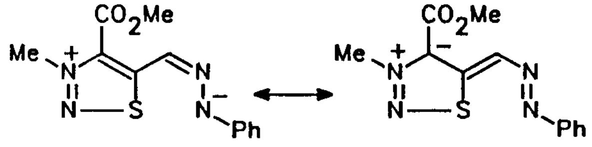
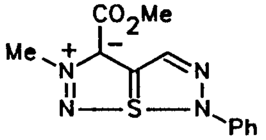
In previous papers we have reported the synthesis of **1** and **2** by methylation of the corresponding 1,2,3-thiadiazole-5-carbaldehyde *N*-phenylhydrazones [1,2]. Compound **1** was characterized as a 6aλ^4-thia-1,2,5,6-tetraazapentalene since the X-ray crystal structure analysis indicates a "stretched" S-NMe bond (1.78 Å) and a short S...NPh distance (1.97 Å) along with a nearly linear N-S...N arrangement (168°). The mesoionic compound **2**, on the other hand, was described as a resonance hybrid of **A** and **B** rather than the thiapentalene structure **2C** on the basis of nmr and X-ray analyses. Indeed, the S-N length (1.70 Å) of **2** is normal for a covalent bond and the long S...NPh distance (2.21 Å), with the *N*-atom lying close to the extended N2-S bond axis (N-S...N 170°), points only to a weak interaction. We have now investigated the influence of benzo-bridging on the structural properties of the corresponding thiapentalenic and/or mesoionic compounds.



1



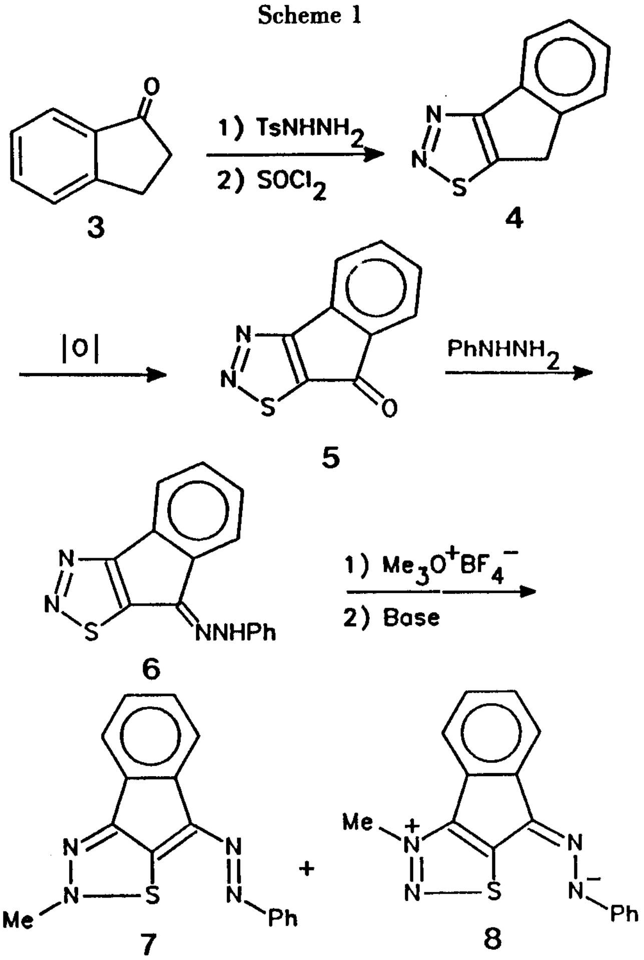
A 2 B



2C

Indanone **3** was converted by the method of Hurd and Mori [3] into the known thiadiazole **4** [4]. This compound was oxidized with potassium dichromate to afford the ketone **5** which was reacted with phenylhydrazine to give the hydrazone **6** (Scheme 1). Methylation of **6** with Meerwein's reagent yielded, after chromatographic separation, a black product (mp 161°, 42%) and a poorly soluble, dark green product (mp 228°, 50%).

Scheme 1



In both cases, methylation has occurred on the thiadiazole ring since the mass spectra were devoid of a $M^{+\cdot}$-N_2 fragment peak typical for thiadiazoles [5]. Instead, fragment ions at m/z 249 for $M^{+\cdot}$-$MeN_2^{\cdot}$ and at m/z 43 for MeN_2^+ were found, suggesting the presence of a *N*-methylated thiadiazole ring. On the basis of their different solubilities and the ^{13}C nmr spectrum of the lower-melting black product (see Experimental) we have assigned structure **7** to the black compound (mp 161°) and structure **8** to the dark green product (mp 228°). These assignments were confirmed by single crystal analyses.

Selected bond lengths for molecule **7** are depicted in Figure 1. We notice that the S-NMe bond (1.735 Å) is shorter, and the S...NPh distance (2.82 Å) much longer than in **1** (1.78 and 1.97 Å respectively). Furthermore, the N-S...N angle is 152.5°, whereas a linear (or approximately linear) arrangement of the atoms is required for the three-center four-electron bonding characteristic of thiapentalenes. The benzo-fusion causes the S1-C5-C6 (137°) and C5-C6-C7 angles (123°) to be much greater than those in **1** (112.5 and 116°), thereby preventing a close approach of N8 to the sulfur atom. Finally, the values for the sequence of bonds N3=C4-C5=C6-N7 are in accord with those found for pyrazole and imidazole [6]. From all these data we conclude that **7** has no thiapentalene character and that there is very little or no contact interaction between S and N8.

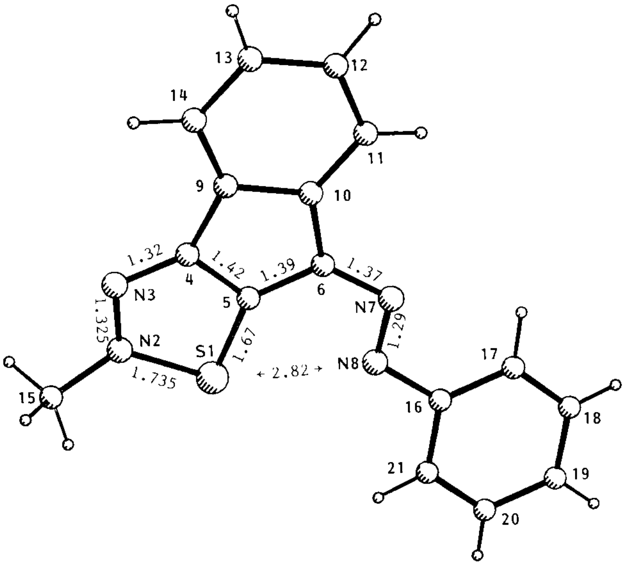


Figure 1. Molecular structure of **7** with numbering scheme and selected bond lengths.

The same conclusion is reached from the X-ray data of compound **8** (Figure 2). Thus, the short covalent S-N bond (1.66 Å) and the long S...NPh distance (3.09 Å), due to the large S1-C5-C6 (141°) and C5-C6-C7 angles (126°), along with the non-linear N-S...N arrangement (155.1°), eliminate any significant S...NPh interaction. This interaction is still present in **2** (S-N 1.70 Å, S...NPh 2.21 Å, N-S...N 170°, S1-C5-C6 120° and C5-C6-C7 119°). The similarity of the C4-C5 and C5-C6 bond lengths (1.40 and 1.41 Å) suggests that the negative charge is delocalized over the conjugated system analogous to **2**.

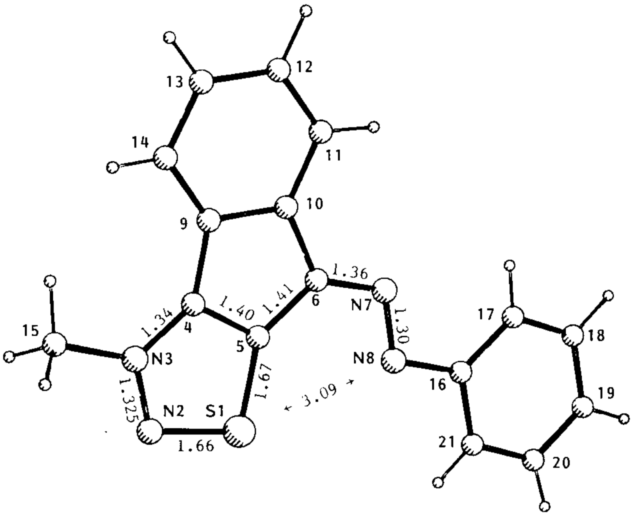


Figure 2. Molecular structure of **8** with numbering scheme and selected bond lengths.

Table 1

Atomic Coordinates (x 10^4, except S1, x 10^5) and Equivalent Temperature Factors ($Å^2$)(x 10^3, S1 x 10^4) of **7**

$$U_{eq} = (1/3)\, \Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \vec{a}_i \vec{a}_j$$

	x/a	y/b	z/c	Ueq
S1	2513(10)	34615(3)	37293(5)	430(3)
N2	-2384(3)	3868(1)	3437(2)	45(1)
N3	-2796(3)	4237(1)	4302(2)	42(1)
C4	-972(4)	4220(1)	5214(2)	39(1)
C5	892(4)	3826(1)	5056(2)	39(1)
C6	2665(4)	3809(1)	6077(2)	40(1)
N7	4569(3)	3416(1)	6206(2)	40(1)
N8	4493(3)	3087(1)	5246(2)	40(1)
C9	-329(4)	4479(1)	6415(2)	40(1)
C10	1920(4)	4222(1)	6942(2)	41(1)
C11	2983(5)	4392(1)	8107(2)	50(1)
C12	1822(6)	4803(1)	8729(3)	58(1)
C13	-370(5)	5043(1)	8207(3)	57(1)
C14	-1479(5)	4884(1)	7047(2)	49(1)
C15	-4167(5)	3766(1)	2350(2)	56(1)
C16	6393(4)	2661(1)	5297(2)	38(1)
C17	8454(4)	2681(1)	6181(2)	41(1)
C18	10252(4)	2267(1)	6113(2)	47(1)
C19	10035(5)	1825(1)	5188(3)	51(1)
C20	7987(5)	1800(1)	4318(2)	51(1)
C21	6182(4)	2216(1)	4363(2)	45(1)

Table 2

Bond Lengths (Å) of **7**

N2-S1	1.735 (2)	C5-S1	1.670 (2)
N3-N2	1.325 (3)	C15-N2	1.456 (3)
C4-N3	1.322 (3)	C5-C4	1.418 (3)
C9-C4	1.454 (3)	C6-C5	1.386 (3)
N7-C6	1.369 (3)	C10-C6	1.460 (3)
N8-N7	1.294 (3)	C16-N8	1.418 (3)
C10-C9	1.432 (3)	C14-C9	1.389 (3)
C11-C10	1.392 (3)	C12-C11	1.394 (4)
C13-C12	1.390 (4)	C14-C13	1.388 (4)
C17-C16	1.398 (3)	C21-C16	1.402 (3)
C18-C17	1.382 (3)	C19-C18	1.388 (4)
C20-C19	1.385 (4)	C21-C20	1.382 (4)

EXPERIMENTAL

8*H*-Indeno[1,2-*d*]-1,2,3-thiadiazole (**4**).

This compound was prepared by Meier *et al.* [4] from the tosylhydrazone of **3** in 8% yield. A higher yield procedure is as follows:

Indanone *N*-tosylhydrazone (54 g, 0.18 mole) is dissolved in thionyl chloride (200 ml) at −60°. The reaction mixture is allowed to come to room temperature, and after 2 hours the precipitate is filtered off, washed with light petroleum and crystallized from ethanol to give **4** in 46% yield (14.5 g), mp 99° (lit [4] 97°).

Note: Longer reaction times result in decreasing yields!

8-Oxo-8*H*-indeno[1,2-*d*]-1,2,3-thiadiazole (**5**).

A mixture of **4** (5 g, 28.7 mmoles) and potassium dichromate (15 g, 51 mmoles) in acetic acid (25 ml) is refluxed overnight with stirring. The reaction mixture is poured into ice-water and extracted three times with dichloromethane (100 ml). The extracts are washed with aqueous sodium hydroxide (10 g in 100 ml) and water (100 ml), and then dried over magnesium sulfate and evaporated to give **5** in 65% yield (3.5 g), mp 124° (ethanol); ir: 1750 (s), 1715 (s), 1610 cm^{-1} (s); ^1H nmr (deuteriochloroform): δ 7.38 (td, 1H, J = 7.5 and 1 Hz), 7.58 (td, 1H, J = 7.5 and 1 Hz), 7.68 (d, 1H, J = 7.5 Hz), 7.76 (d, 1H, J = 7.5 Hz); ^{13}C nmr (deuteriochloroform): δ 121.5, 126.2, 130.1, 135.4, 136.1 and 138.6 (benzo C-atoms), 147.1 (C-8a), 177.1 and 179.2 (C-3a and/or C-8); ms: (%) m/z 188 (10, $M^{+\cdot}$), 160 (100, $M^{+\cdot}$–N_2 or CO), 132 (85, $M^{+\cdot}$–N_2–CO), 93 (38).

Anal. Calcd. for $C_9H_4N_2OS$ (mol wt 188): C, 57.44; H, 2.13. Found: C, 57.26; H, 2.07.

8-(Phenylhydrazono)-8*H*-indeno[1,2-*d*]-1,2,3-thiadiazole (**6**).

Phenylhydrazine (0.53 g, 5 mmoles) is added to a hot solution of **5** (0.94 g, 5 mmoles) in ethanol (10 ml) and the reaction mixture is allowed to stand overnight at room temperature. Compound **6** crystallizes out as the hemihydrate in 81% yield (1.16 g), mp 169°; ir: 3410 (br), 3210 (m), 1560 cm^{-1} (s); ^1H nmr (dimethyl sulfoxide-d_6): δ 7.10 (t, 1H), 7.38-7.63 (two m, 6H), 7.98 (m, 2H), 11.2 (br s, NH); ^{13}C nmr (dimethyl sulfoxide-d_6): δ 115.0, 122.8, 129.2 and 143.5 (Ph C-atoms), 120.1, 121.0, 127.8, 127.9, 128.9 and 141.7 (benzo C-atoms), 129.4 (C-8), 136.6 (C-8a), 169.2 (C-3a); ms: (%) m/z 278 (100, $M^{+\cdot}$), 250 (65, $M^{+\cdot}$–N_2), 249 (72), 218 (35, $M^{+\cdot}$–N_2–S), 114 (20), 92 (81, $PhNH^+$), 91 (58, $PhN^{+\cdot}$).

Anal. Calcd. for $C_{15}H_{10}N_4S \cdot ½H_2O$ (mol wt 287): C, 62.71; H, 3.83. Found: C, 62.76; H, 3.97.

Table 3

Bond Angles (°) of **7**

C5 -S1 -N2	87.9 (1)	N3 -N2 -S1	116.5 (2)
C15 -N2 -S1	122.6 (2)	C15 -N2 -N3	120.6 (2)
C4 -N3 -N2	109.0 (2)	C5 -C4 -N3	115.4 (2)
C9 -C4 -N3	137.3 (2)	C9 -C4 -C5	107.2 (2)
C4 -C5 -S1	111.1 (2)	C6 -C5 -S1	137.3 (2)
C6 -C5 -C4	111.4 (2)	N7 -C6 -C5	123.4 (2)
C10 -C6 -C5	106.1 (2)	C10 -C6 -N7	130.2 (2)
N8 -N7 -C6	110.8 (2)	C16 -N8 -N7	114.9 (2)
C10 -C9 -C4	106.3 (2)	C14 -C9 -C4	132.2 (2)
C14 -C9 -C10	121.5 (2)	C9 -C10 -C6	109.0 (2)
C11 -C10-C6	132.0 (2)	C11 -C10 -C9	119.0 (2)
C12 -C11-C10	119.1 (3)	C13 -C12 -C11	121.1 (3)
C14 -C13-C12	121.3 (3)	C13 -C14 -C9	118.0 (3)
C17 -C16-N8	124.3 (2)	C21 -C16 -N8	116.5 (2)
C21 -C16-C17	119.2 (2)	C18 -C17 -C16	119.7 (2)
C19 -C18-C17	121.1 (2)	C20 -C19 -C18	119.4 (2)
C21 -C20-C19	120.4 (2)	C20 -C21 -C16	120.3 (2)

Table 4

Atomic Coordinates (x 10^4, except S1, x 10^5) and Equivalent Temperature Factors (Å^2)(x 10^3, S1 x 10^4) of **8**

$$U_{eq} = (1/3)\, \Sigma_i \Sigma_j U_{ij} a^*_i a^*_j \vec{a}_i \vec{a}_j$$

	x/a	y/b	z/c	Ueq
S1	42864(3)	18722(7)	3897(4)	520(4)
N2	4736(1)	2990(2)	1281(1)	56(1)
N3	5277(1)	3558(2)	1203(1)	46(1)
C4	5355(1)	3146(2)	468(1)	42(1)
C5	4816(1)	2165(2)	-87(1)	40(1)
C6	4908(1)	1751(2)	-854(1)	39(1)
N7	4488(1)	816(2)	-1544(1)	40(1)
N8	3974(1)	277(2)	-1426(1)	42(1)
C9	5826(1)	3394(2)	70(1)	41(1)
C10	5538(1)	2517(2)	-752(1)	40(1)
C11	5882(1)	2497(3)	-1294(2)	50(1)
C12	6497(1)	3304(3)	-1010(2)	62(1)
C13	6781(1)	4143(3)	-198(2)	60(1)
C14	6442(1)	4201(3)	341(2)	51(1)
C15	5750(1)	4584(3)	1929(2)	60(1)
C16	3523(1)	-692(2)	-2131(1)	41(1)
C17	3581(1)	-1037(3)	-2922(2)	49(1)
C18	3097(1)	-1978(3)	-3573(2)	58(1)
C19	2550(1)	-2598(3)	-3452(2)	57(1)
C20	2495(1)	-2272(3)	-2673(2)	59(1)
C21	2978(1)	-1328(3)	-2010(2)	51(1)

Methylation of **6**.

A mixture of **6** (0.8 g, 2.87 mmoles) and trimethyloxonium tetrafluoroborate (0.9 g, 6 mmoles) in dichloromethane (60 ml) is stirred overnight at room temperature. After removal of the solvent, the residue is treated with methanol (60 ml) and aqueous potassium carbonate (3 g in 100 ml) and then extracted three times with dichloromethane (100 ml). The extracts are washed twice with water (100 ml), dried over magnesium sulfate and chromatographed on silica gel with dichloromethane/light petroleum (first 1:1, then 1:0) as the eluent to give **7** and **8**.

2-Methyl-8-(phenylazo)-2*H*-indeno[1,2-*d*]-1,2,3-thiadiazole (**7**).

This compound is obtained as black crystals in 42% yield (350 mg), mp 161°; ^{1}H nmr (deuteriochloroform): δ 4.10 (s, 3H, CH_3), 7.2-7.3 (m, 2H), 7.43 (t, 2H), 7.50 (td, 1H), 7.85 (d, 2H), 8.01 and 8.12 (two d, 2H); ^{13}C nmr (deuteriochloroform): δ 42.1 (CH_3, $^1J_{CH}$ = 142 Hz), 118.3, 121.4, 122.7, 126.3, 128.1 and 141.9 (benzo C-atoms), 121.3, 127.9, 129.0 and 153.3 (Ph C-atoms), 125.6 (C-8a), 132.9 and 152.0 (C-3a and/or C-8); ms: (%) m/z 292 (92, $M^{+\cdot}$), 249 (100, $M^{+\cdot}$-MeN_2), 158 (16), 146 (15), 114 (14), 91 ($PhN^{+\cdot}$), 77 (13, Ph^+), 43 (7, MeN_2^+).

Anal. Calcd. for $C_{16}H_{12}N_4S$ (mol wt 292): C, 65.73; H, 4.14. Found: C, 65.51; H, 4.18.

2-(3-Methyl-8*H*-indeno[1,2-*d*]-1,2,3-thiadiazol-3-ium-8-ylidene)-1-phenylhydrazin-1-ide (**8**).

This compound is obtained as dark green crystals in 50% yield (420 mg), mp 228°; insufficiently soluble for nmr analysis; ms: (%) m/z 292 (100, $M^{+\cdot}$), 249 (53, $M^{+\cdot}$-MeN_2), 221 (35, m/z 249-N_2), 187 (90, $M^{+\cdot}$-PhN_2), 146 (34), 114 (47), 91 (26, $PhN^{+\cdot}$), 77 (37, Ph^+), 43 (33, MeN_2^+).

Anal. Calcd. for $C_{16}H_{12}N_4S$ (mol wt 292): C, 65.73; H, 4.14. Found: C, 65.49; H, 4.27.

Table 5

Bond Lengths (Å) of **8**

N2 -S1	1.661 (2)	C5 -S1	1.671 (2)
N3 -N2	1.325 (3)	C4 -N3	1.344 (3)
C15 -N3	1.472 (3)	C5 -C4	1.398 (3)
C9 -C4	1.452 (3)	C6 -C5	1.412 (3)
N7 -C6	1.357 (3)	C10 -C6	1.451 (3)
N8 -N7	1.296 (2)	C16 -N8	1.408 (2)
C10 -C9	1.430 (3)	C14 -C9	1.383 (3)
C11 -C10	1.396 (3)	C12 -C11	1.379 (3)
C13 -C12	1.401 (4)	C14 -C13	1.382 (4)
C17 -C16	1.399 (3)	C21 -C16	1.391 (3)
C18 -C17	1.378 (3)	C19 -C18	1.388 (4)
C20 -C19	1.372 (4)	C21 -C20	1.387 (3)

Crystal Structure Analysis of **7**.

Compound **7** crystallizes in the space group $P2_1/c$ with a = 5.933(1), b = 20.618(3), c = 11.566(2) Å, β = 103.55(2)°, V = 1375.4(4) Å^3, Z = 4, D_x = 1.41 gcm^{-3}. Intensities from a parallelepiped crystal 0.21 x 0.33 x 0.57 mm were measured using a Huber 4-circle diffractometer with graphite-monochromatized MoKα radiation (λ = 0.7169 Å). Of the 3161 independent reflections with $\sin\theta/\lambda \leq 0.64$ Å^{-1}, 2297 had $I \geq 2.5\sigma(I)$ and were considered as observed. The structure was solved by direct methods (SHELXS-86) [7] and refined by least squares methods [8] to an R-value of 0.043 for the observed reflections. Atomic coordinates, bond lengths and angles are given in Tables 1,2 and 3. Figure 1 shows a view of the molecule with an arbitrary not systematic numbering scheme and selected bond lengths.

Table 6

Bond Angles (°) of **8**

C5 -S1 -N2	94.5 (1)	N3 -N2 -S1	108.6 (2)
C4 -N3 -N2	117.5 (2)	C15 -N3 -N2	117.5 (2)
C15 -N3 -C4	125.0 (2)	C5 -C4 -N3	110.4 (2)
C9 -C4 -N3	139.9 (2)	C9 -C4 -C5	109.7 (2)
C4 -C5 -S1	109.0 (2)	C6 -C5 -S1	141.6 (2)
C6 -C5 -C4	109.4 (2)	N7 -C6 -C5	126.5 (2)
C10 -C6 -C5	106.2 (2)	C10 -C6 -N7	127.3 (2)
N8 -N7 -C6	112.4 (2)	C16 -N8 -N7	114.2 (2)
C10 -C9 -C4	104.8 (2)	C14 -C9 -C4	133.8 (2)
C14 -C9 -C10	121.3 (2)	C9 -C10 -C6	109.8 (2)
C11 -C10 -C6	131.2 (2)	C11 -C10 -C9	119.0 (2)
C12 -C11 -C10	118.8 (2)	C13 -C12 -C11	121.9 (2)
C14 -C13 -C12	120.3 (2)	C13 -C14 -C9	118.7 (2)
C17 -C16 -N8	125.5 (2)	C21 -C16 -N8	115.5 (2)
C21 -C16 -C17	119.0 (2)	C18 -C17 -C16	120.0 (2)
C19 -C18 -C17	120.7 (3)	C20 -C19 -C18	119.4 (2)
C21 -C20 -C19	120.7 (2)	C20 -C21 -C16	120.2 (2)

Crystal Structure Analysis of **8**.

Compound **8** crystallizes in the space group C2/c with a = 21.520(4), b = 8.704(1), c = 16.493(2) Å, β = 116.84(2)°, V = 2756.5(7) Å^3, Z = 8, D_x = 1.41 gcm^{-3}. Intensities from a parallelepiped crystal 0.2 x 0.4 x 0.6 mm were measured using a Huber diffractometer with graphite monochromatized CuKα radiation (λ = 1.54178 Å). Of the 2481 independent reflections with $\sin\theta/\lambda$ $\leq$ 0.6 Å^{-1}, 2304 had $I \geq 2.5\sigma(I)$ and were considered as observed. The structure was solved by direct methods (SHELXS-86) [7] and refined by least squares methods [8] to an R-value of 0.063 for the observed reflections. Atomic coordinates, bond lengths and angles are given in Tables 4,5 and 6. Figure 2 shows the molecule with an arbitrary not systematic numbering scheme and selected bond lengths.

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