

## Formation and X-Ray Analysis of an Aza-dihydrotriquinacene Derivative from 4-Cyano-1-methyl-1,2-dihydropyridine

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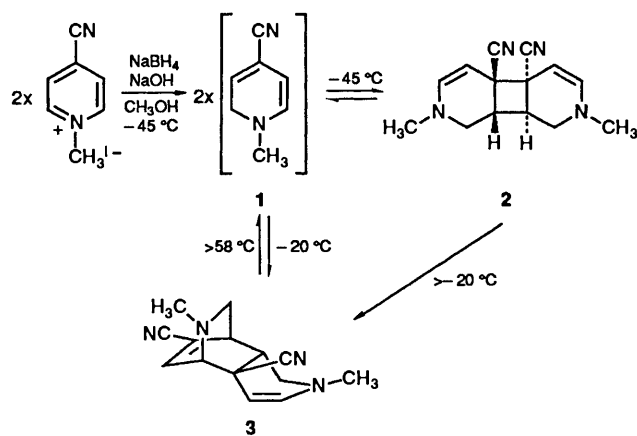
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4-Cyano-1-methyl-1,2-dihydropyridine **1** is a highly activated captodative diene known to cyclodimerize, even at  $-45^\circ\text{C}$ , in a [2 + 2] mode to **2** which isomerizes above  $-20^\circ\text{C}$  to the [4 + 2] dimer **3**. Compound **3** is now found to equilibrate above  $\sim 50^\circ\text{C}$  with the monomer **1**. In addition **3** furnishes, with dimethyl acetylenedicarboxylate in boiling acetone, the expected [2 + 2] adduct **7** along with the title compound, a surprising 2:1 adduct **6** of dimethyl acetylenedicarboxylate and **1**. Both new structures **6** and **7** are proven by X-ray analysis.

The crystals of **6** ( $\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_8$ ) are monoclinic, space group  $P2_1/n$ ,  $Z = 4$ , with  $a = 13.818(2)$ ,  $b = 10.994(2)$ ,  $c = 13.128(2)$  Å,  $\beta = 100.09(1)^\circ$ ,  $V = 1963.4(5)$  Å<sup>3</sup>. Using 2754 independent reflections with  $I \geq 2.5\sigma(I)$  the structure was refined to  $R = 0.054$ . The crystals of **7** ( $\text{C}_{20}\text{H}_{22}\text{N}_4\text{O}_4$ ) are also monoclinic, space group  $P2_1/c$ ,  $Z = 8$ , with  $a = 20.229(7)$ ,  $b = 11.307(3)$ ,  $c = 18.199(4)$  Å,  $\beta = 103.73(2)^\circ$ ,  $V = 4044(2)$  Å<sup>3</sup>. This second structure was refined to  $R = 0.058$  using 2718 observed reflections.

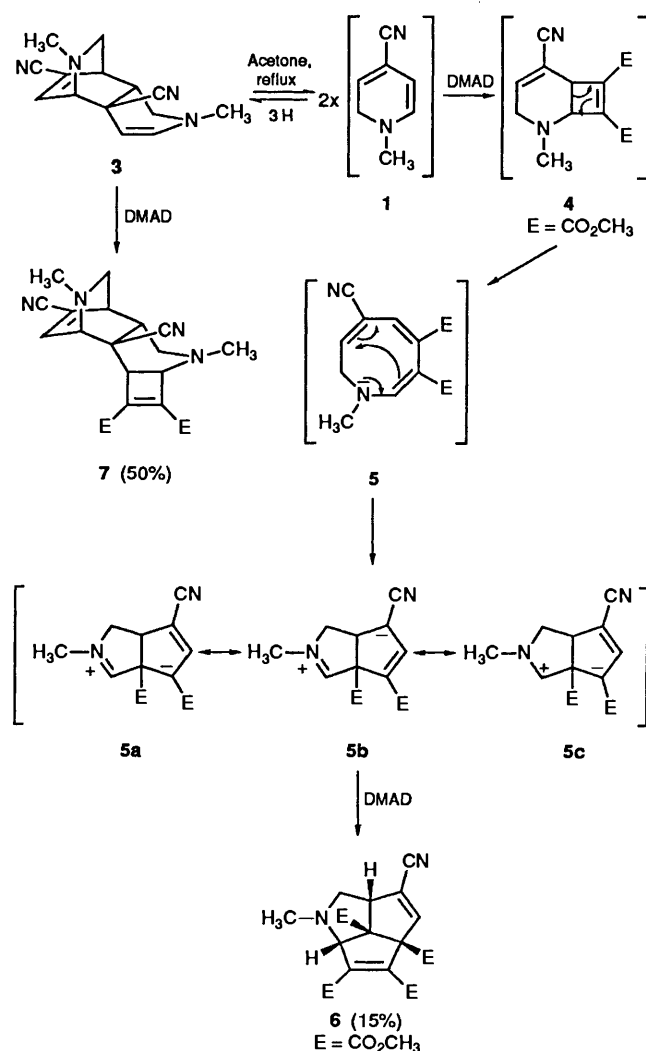
4-Cyano-1-methyl-1,2-dihydropyridine **1** shows its captodative (cd)<sup>1</sup> diene character by an exceptional reactivity. It is known<sup>2</sup> that **1** forms, at  $-45^\circ\text{C}$ , the [2 + 2] cycloadduct **2** which isomerizes above  $-20^\circ\text{C}$  to the [4 + 2] dimer **3** (Scheme 1).



Scheme 1

Even when refluxing in acetone, **3** is in equilibrium with the monomer **1**. Its intramolecular [4 + 2] trapping has been described elsewhere.<sup>3</sup> We have also reported in an earlier communication<sup>4</sup> the intermolecular cycloaddition, especially with cd alkenes.

In this paper we describe the surprising twofold reaction of dimethyl acetylenedicarboxylate (DMAD) with **1** leading to the azadihydro triquinacene **6**.<sup>\*</sup> The reaction probably proceeds *via* the dihydroazocine **5** which, after an intramolecular Michael addition yielding the 1,3-dipole **5c** reacts with another equivalent of DMAD to afford **6** in 15% yield (Scheme 2). Furthermore, 50% of **7**, a 1:1 adduct of **3** and DMAD, is



Scheme 2

\* **6**: Tetramethyl 3-cyano-1-methyl-1,2,2a,4a,6a,6b-hexahydro-penteno[b,c]pyrrole-4a,5,6,6b-tetracarboxylate.

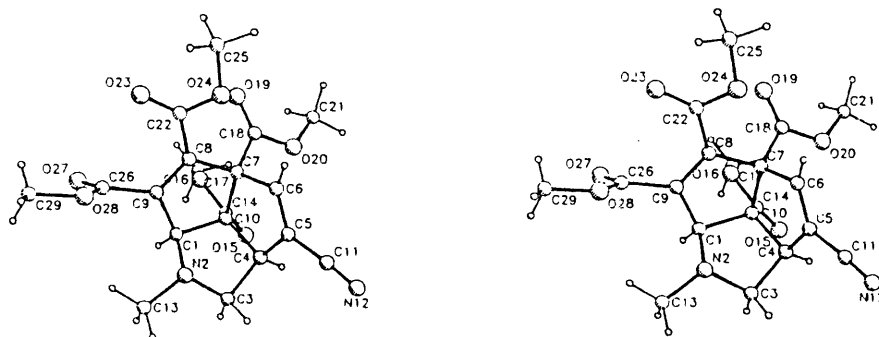


Fig. 1 Stereoscopic view of molecule 6

Table 1 Data collection and refinement parameters

	Compound 6	Compound 7
Formula	C <sub>19</sub> H <sub>20</sub> N <sub>2</sub> O <sub>8</sub>	C <sub>20</sub> H <sub>22</sub> N <sub>4</sub> O <sub>4</sub>
Crystal system	monoclinic	monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> /Å	13.818(2)	20.229(7)
<i>b</i> /Å	10.994(2)	11.307(3)
<i>c</i> /Å	13.128(2)	18.199(4)
$\beta$ /°	100.09(1)	103.73(2)
<i>U</i> /Å <sup>3</sup>	1963.4(5)	4044(2)
<i>Z</i>	4	8
Approximate crystal size/mm	0.35 × 0.22 × 0.40	0.20 × 0.32 × 0.36
Collection range (sin $\theta$ / $\lambda$ )max Å <sup>-1</sup>	0.62	0.60
Range of <i>hkl</i>	-16 ≤ <i>h</i> ≤ 16 0 ≤ <i>k</i> ≤ 13 0 ≤ <i>l</i> ≤ 16	-23 ≤ <i>h</i> ≤ 23 0 ≤ <i>k</i> ≤ 12 0 ≤ <i>l</i> ≤ 20
Scans	$\omega$	$\theta$ -2 $\theta$
Indices of standard reflection	4 1 - 6	5 1 - 1
Measured reflections	3860	7127
Observed reflections [ <i>I</i> > 2.5 $\sigma$ ( <i>I</i> )]	2754	2718
Parameters	304	507
<i>R</i>	0.054	0.058
<i>wR</i>	0.067	0.054
$w = 1/(\sigma^2 + gF^2)$ <i>g</i> =	0.005 07	0.000 30
<i>S</i>	1.12	1.53
( $\Delta$ / $\sigma$ )	0.26	0.04
$\Delta\rho$ (max, min)/e Å <sup>-3</sup>	0.32, -0.23	0.35, -0.26

obtained.\* Both new structures (6 and 7) are characterized by <sup>1</sup>H and <sup>13</sup>C NMR, IR and mass spectrometry and are proven by X-ray analysis as described in the following discussion.

### Experimental

The <sup>1</sup>H NMR spectra were recorded on a Gemini-200 (200 MHz) spectrometer. The <sup>13</sup>C NMR spectra were recorded on a Gemini-200 (50 MHz) spectrometer (*J*-values are given in Hz). The samples were dissolved in CDCl<sub>3</sub> with tetramethylsilane (TMS) as internal standard. The following abbreviations are used: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; b, broad. IR and mass spectra were recorded on a Nicolet-205 and Varian-445SEI apparatus respectively. Melting points were determined on a Dr. Tottoli apparatus and are uncorrected.

**Preparation of 6 and 7.**—DMAD (1.5 g; 10.5 mmol) was added dropwise to a refluxing solution of 3 (1 g; 4.16 mmol) in

acetone (50 cm<sup>3</sup>). After the addition, the mixture was refluxed for 3 h under an atmosphere of nitrogen. The acetone was evaporated off under reduced pressure. Column chromatography of the black residue over silica gel (eluent: diethyl ether) gave 6 (0.49 g; 15%; m.p. 115 °C; *R*<sub>f</sub> = 0.70 in diethyl ether) and 7 (0.79 g; 50%; m.p. 142 °C; *R*<sub>f</sub> = 0.35–0.40 in diethyl ether). Both products were recrystallized from chloroform-ether (1:10).

**Spectral properties of 6**  $\delta$ <sub>H</sub> 2.37 (3 H, s), 2.94 (1 H, dd, *J* 10.3, *J* 6.3), 3.69 (3 H, s), 3.74 (3 H, s), 3.80 (3 H, s), 3.84 (3 H, s), 4.25 (1 H, s); 6.83 (1 H, d, *J* 1.6), (one proton signal is hidden under the four methyl peaks between 3.69 and 3.84);  $\delta$ <sub>C</sub> 40.5 (q, *J* 134.8), 52.3 (q, *J* 148.6), 52.8 (q, *J* 148.6), 53.7 (dd, *J* 143.4, *J* 8.4), 61.1 (td, *J* 140.0, *J* 4), 72.1 (sm), 75.9 (sdd, *J* 5.4, *J* 5.5), 78.8 (dm, *J* 144), 114.2 (sd, *J* 4.6), 118.6 (sd, *J* 4.4), 137.1 (sd, *J* 4.8), 142.6 (sd, *J* 2), 145.7 (dd, *J* 179.8, *J* 4.6), 163.1 (sd, *J* 4.0), 164.5 (sd, *J* 3.7), 169.0 (sd, *J* 3.6), 170.6 (sd, *J* 4.3);  $\nu$ <sub>max</sub>(KBr)/cm<sup>-1</sup> 1620, 1663 (C=C), 1733, 1736, 1743, 1755 (C=O), 2224 (CN), 2843, 2956 (C-H); *m/z* (EI) 43.0, 82.9, 145.0, 203.8, 286.1 [*M*<sup>+</sup> - (2 × CO<sub>2</sub>CH<sub>3</sub>)], 345.2 (*M*<sup>+</sup> - CO<sub>2</sub>CH<sub>3</sub>), 372.1 (*M*<sup>+</sup> - CH<sub>3</sub>OH), 404 (*M*<sup>+</sup>).

**Spectral properties of 7**  $\delta$ <sub>H</sub> 1.90 (2 H, bm), 2.36 (3 H, s), 2.44 (3 H, s), 2.64 (1 H, s), 2.83 (2 H, bm), 3.41 (2 H, d, *J* 9.7), 3.81 (3 H, s), 3.87 (3 H, s), 7.13 (1 H, bm);  $\delta$ <sub>C</sub> 38 (b), 41 (b), 43.55 (d, *J* 136.4), 44.15 (q, *J* 135.4), 44.28 (q, *J* 134.0), 52.06 (q, *J* 147.8), 52.24 (q, *J* 147.9), 55.05 (tm, *J* 141.4), 61 (bdm, *J* 160.0), 116.07 (s), 118 (b), 122.17 (s), 142 (b), 144 (b), 147 (b), 161.18 (sd, *J* 4.4);  $\nu$ <sub>max</sub>(KBr)/cm<sup>-1</sup> 1639, 1649 (C=C), 1720, 1723 (C=O), 2217, 2234 (CN), 2853, 2885, 2904, 2917, 2944, 2971 (C-H); *m/z* (EI) 119 (4-cyano-1-methylpyridinium), 120 (4-cyano-1-methyl-1,2-dihydropyridine), 202.9, 230.8, 323.0, 350.9 (*M*<sup>+</sup> - CH<sub>3</sub>OH), 382 (*M*<sup>+</sup>).

**Preparation of 7.** Compound 3 (2 g, 8.32 mmol) and DMAD (3 g, 21.11 mmol) were dissolved in acetone (50 cm<sup>3</sup>). The mixture was stirred at room temperature for two weeks under an atmosphere of nitrogen. The acetone was evaporated off under reduced pressure and column chromatography over silica gel (eluent: diethyl ether) afforded 7 (2.5 g, 78%, m.p. 142 °C, *R*<sub>f</sub> = 0.35–0.40).

**X-Ray Determination.**—Crystals of both compounds were obtained by slow evaporation from chloroform-diethyl ether (1:10). The data collection and refinement parameters are summarized in Table 1. The lattice parameters were refined using 18 reflections for 6 and 23 reflections for 7 in the range 4° ≤ 2 $\theta$  ≤ 26°. A Huber four circle diffractometer, monochromatized Mo-K $\alpha$  was used for both 6 and 7. One standard reflection was checked every 50 reflections; no significant deviation was found. Both structures were solved by SHELXS86<sup>5</sup> and refined by SHELX76.<sup>6</sup> For compound 6 hydrogen atoms were located from a difference Fourier synthesis, except those of the methyl groups C(13), C(17), C(21) and C(25), which were calculated (C-H = 1.09 Å, H-C-H = 109.5°); for compound

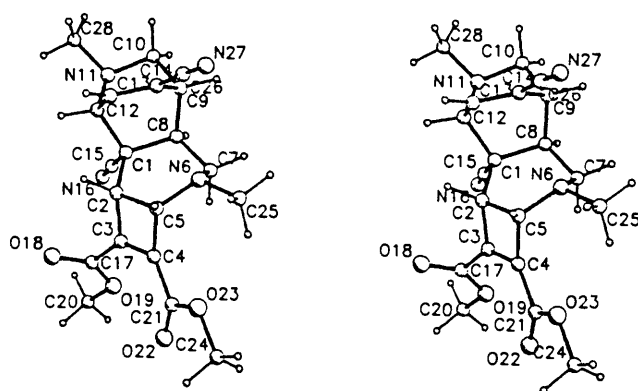
\* 7: Dimethyl 7b,8-dicyano-2,5-dimethyl-1,2,3,3a,4,5,5a,7a,7b-octahydro-1,3-etheno-1*H*-cyclobuteno[*b*]pyrrolo[3,4-*d*]pyridine-6,7-dicarboxylate.

**Table 2** Atomic coordinates ( $\times 10^4$ )

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
<b>Compound 6</b>			
C(1)	8 647(2)	730(2)	7 638(2)
N(2)	9 357(2)	-40(2)	8 314(2)
C(3)	9 872(2)	-750(3)	7 621(2)
C(4)	10 066(2)	189(2)	6 822(2)
C(5)	10 906(2)	1 045(2)	7 189(2)
C(6)	10 652(2)	2 201(3)	7 225(2)
C(7)	9 554(2)	2 381(2)	6 914(2)
C(8)	9 047(2)	2 821(2)	7 791(2)
C(9)	8 533(2)	1 941(2)	8 132(2)
C(10)	9 166(2)	1 042(3)	6 707(2)
C(11)	11 899(2)	582(3)	7 441(2)
N(12)	12 657(2)	157(3)	7 646(2)
C(13)	8 918(3)	-805(3)	9 023(3)
C(14)	8 465(2)	856(2)	5 689(2)
O(15)	8 545(2)	81(2)	5 070(2)
O(16)	7 734(1)	1 663(2)	5 598(1)
C(17)	7 004(2)	1 589(3)	4 664(2)
C(18)	9 318(2)	3 217(2)	5 970(2)
O(19)	8 853(2)	4 134(2)	5 935(2)
O(20)	9 715(2)	2 766(2)	5 197(1)
C(21)	9 529(3)	3 399(4)	4 215(2)
C(22)	9 138(2)	4 066(2)	8 221(2)
O(23)	8 551(2)	4 526(2)	8 672(2)
O(24)	9 973(1)	4 596(2)	8 080(2)
C(25)	10 116(3)	5 840(3)	8 449(3)
C(26)	7 760(3)	2 075(3)	8 820(3)
O(27)	6 893(2)	2 056(3)	8 496(3)
O(28)	8 157(2)	2 124(3)	9 813(2)
C(29)	7 448(5)	2 218(6)	10 508(4)
C(26')	8 297(9)	2 082(9)	9 248(10)
O(27')	8 824(8)	2 225(8)	10 064(7)
O(28')	7 367(9)	1 908(10)	9 089(10)
C(29')	6 896(15)	1 984(18)	10 033(15)
<b>Compound 7</b>			
<b>Molecule A</b>			
C(1)	8 633(2)	3 130(4)	3 433(3)
C(2)	8 913(2)	3 159(4)	4 314(3)
C(3)	8 940(3)	2 014(4)	4 751(3)
C(4)	9 613(3)	2 058(5)	5 050(3)
C(5)	9 711(2)	3 221(5)	4 648(3)
N(6)	10 106(2)	3 250(4)	4 086(3)
C(7)	9 854(3)	2 415(5)	3 473(3)
C(8)	9 183(3)	2 874(5)	2 974(3)
C(9)	9 286(3)	4 014(5)	2 558(3)
C(10)	8 626(3)	4 257(6)	1 949(3)
N(11)	8 057(2)	4 247(4)	2 328(2)
C(12)	8 300(3)	4 340(5)	3 154(3)
C(13)	8 846(3)	5 265(5)	3 387(3)
C(14)	9 382(3)	5 057(5)	3 092(3)
C(15)	8 102(3)	2 206(5)	3 248(3)
N(16)	7 703(3)	1 466(5)	3 112(3)
C(17)	8 352(3)	1 314(5)	4 879(3)
O(18)	7 850(2)	1 788(3)	4 986(2)
O(19)	8 445(2)	164(3)	4 853(2)
C(20)	7 856(3)	-565(5)	4 903(4)
C(21)	10 044(2)	1 369(5)	5 677(3)
O(22)	9 865(2)	486(4)	5 948(2)
O(23)	10 649(2)	1 886(3)	5 929(2)
C(24)	11 110(3)	1 332(6)	6 573(3)
C(25)	10 845(3)	3 147(8)	4 415(4)
C(26)	10 001(3)	5 738(6)	3 278(3)
N(27)	10 503(3)	6 254(5)	3 439(3)
C(28)	7 527(3)	5 120(8)	2 005(4)
<b>Molecule B</b>			
C(1)	6 741(2)	5 562(5)	4 587(3)
C(2)	6 052(2)	5 884(4)	4 019(3)
C(3)	6 048(2)	6 911(5)	3 498(3)
C(4)	5 912(3)	6 255(5)	2 865(3)
C(5)	5 854(3)	5 116(5)	3 287(3)
N(6)	6 338(2)	4 151(4)	3 273(2)
C(7)	6 425(3)	3 507(5)	3 994(3)

**Table 2** (continued)

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
<b>Molecule B</b>			
C(8)	6 894(3)	4 185(4)	4 623(3)
C(9)	6 885(3)	3 737(5)	5 416(3)
C(10)	7 478(3)	4 326(6)	5 992(3)
N(11)	7 418(2)	5 623(5)	5 885(2)
C(12)	6 741(3)	5 970(5)	5 407(3)
C(13)	6 170(3)	5 326(6)	5 641(3)
C(14)	6 238(3)	4 159(6)	5 623(3)
C(15)	7 302(3)	6 162(5)	4 342(3)
N(16)	7 718(2)	6 646(4)	4 129(3)
C(17)	6 130(3)	8 191(6)	3 683(4)
O(18)	6 281(2)	8 542(4)	4 319(3)
O(19)	6 023(2)	8 853(4)	3 067(3)
C(20)	6 134(5)	10 131(6)	3 184(6)
C(21)	5 810(4)	6 511(7)	2 051(4)
O(22)	6 025(4)	7 343(6)	1 799(3)
O(23)	5 508(3)	5 717(5)	1 633(3)
C(24)	5 412(8)	5 829(11)	815(4)
C(25)	6 079(3)	3 352(5)	2 620(3)
C(26)	5 761(3)	3 311(6)	5 799(3)
N(27)	5 379(3)	2 635(6)	5 925(3)
C(28)	7 603(4)	6 262(7)	6 605(4)

**Fig. 2** Stereoscopic view of molecule 7A

7 all the H atoms were introduced in idealized positions. H atoms were refined with an isotropic common temperature factor. During the refinement process of **6**, a second position was observed for the methoxycarbonyl substituent on C(9). The atoms of this second position, labelled with primes, were included with isotropic temperature factors and their occupation was refined. At the end of the refinement, the occupation factors for the two positions converged to 0.74 and 0.26 respectively. Atomic scattering factors were taken from International Tables for X-ray Crystallography, vol. IV, 1974.<sup>7</sup>

### Discussion

Positional coordinates are given in Table 2. Figs. 1 and 2 are stereoscopic views of the molecules, showing the numbering of the atoms (program PLUTO).<sup>8</sup> Bond distances and angles are given in Tables 3 and 4.

In **6**, two of the five-membered rings of the tricyclic system have significant deviations from planarity. The pentene ring C(1)–C(10)–C(7)–C(8)–C(9) adopted a flat half-chair conformation with endocyclic torsion angles of 14(1), -12(1), 5(1), 5(1), -12(1)°, probably to minimize the non-bonded repulsion between the four adjacent methoxycarbonyl substituents. This steric hindrance is also reflected by the angles C(22)–C(8)–C(9), 124.2(2)° and C(26)–C(9)–C(8), 127.2(3)°.

Table 3 Bond distances/Å

Bond	Distance/Å	Bond	Distance/Å
<b>Compound 6</b>			
N(2)-C(1)	1.470(3)	C(9)-C(1)	1.501(3)
C(10)-C(1)	1.560(3)	C(3)-N(2)	1.473(4)
C(13)-N(2)	1.463(3)	C(4)-C(3)	1.528(4)
C(5)-C(4)	1.506(3)	C(10)-C(4)	1.544(3)
C(6)-C(5)	1.322(4)	C(11)-C(5)	1.446(3)
C(7)-C(6)	1.514(3)	C(8)-C(7)	1.527(3)
C(10)-C(7)	1.574(3)	C(18)-C(7)	1.531(3)
C(9)-C(8)	1.323(3)	C(22)-C(8)	1.478(3)
C(26)-C(9)	1.523(5)		
C(14)-C(10)	1.521(3)	N(12)-C(11)	1.135(3)
O(15)-C(14)	1.195(3)	O(16)-C(14)	1.334(3)
C(17)-O(16)	1.446(3)	O(19)-C(18)	1.192(3)
O(20)-C(18)	1.331(3)	C(21)-O(20)	1.448(3)
O(23)-C(22)	1.197(3)	O(24)-C(22)	1.335(3)
C(25)-O(24)	1.454(3)	O(27)-C(26)	1.199(5)
O(28)-C(26)	1.324(5)	C(29)-O(28)	1.455(5)
<b>Compound 7</b>			
	<b>Molecule A</b>	<b>Molecule B</b>	
C(2)-C(1)	1.568(8)	1.569(6)	
C(8)-C(1)	1.569(8)	1.586(7)	
C(12)-C(1)	1.557(7)	1.562(7)	
C(15)-C(1)	1.480(7)	1.477(8)	
C(3)-C(2)	1.514(7)	1.498(8)	
C(5)-C(2)	1.585(6)	1.560(7)	
C(4)-C(3)	1.342(7)	1.342(8)	
C(17)-C(3)	1.491(8)	1.487(9)	
C(5)-C(4)	1.540(7)	1.518(8)	
C(21)-C(4)	1.482(7)	1.475(9)	
N(6)-C(5)	1.442(7)	1.470(7)	
C(7)-N(6)	1.457(7)	1.475(7)	
C(25)-N(6)	1.477(6)	1.486(7)	
C(8)-C(7)	1.533(7)	1.511(7)	
C(9)-C(8)	1.534(8)	1.534(7)	
C(10)-C(9)	1.545(7)	1.544(7)	
C(14)-C(9)	1.511(8)	1.522(8)	
N(11)-C(10)	1.476(8)	1.481(9)	
C(12)-N(11)	1.469(6)	1.490(6)	
C(28)-N(11)	1.472(9)	1.465(8)	
C(13)-C(12)	1.506(7)	1.508(8)	
C(14)-C(13)	1.341(9)	1.328(9)	
C(26)-C(14)	1.441(8)	1.449(9)	
N(16)-C(15)	1.148(8)	1.147(8)	
O(18)-C(17)	1.205(7)	1.193(9)	
O(19)-C(17)	1.317(7)	1.322(9)	
C(20)-O(19)	1.470(7)	1.470(8)	
O(22)-C(21)	1.207(7)	1.175(11)	
O(23)-C(21)	1.336(7)	1.238(9)	
C(24)-O(23)	1.454(6)	1.460(9)	
N(27)-C(26)	1.148(8)	1.147(10)	

which are significantly greater than the normal  $sp^2$  value, and by the torsion of the two substituents out of the ethylenic bond plane:  $C(7)-C(8)-C(22)-O(24) = 25(1)^\circ$  and  $C(8)-C(9)-C(26)-O(28) = 84(1)^\circ$ . An half-chair conformation with torsion angles of  $43(1)$ ,  $-33(1)$ ,  $14(1)$ ,  $12(1)$ ,  $-34(1)^\circ$ , respectively is observed for the pyrrolidine ring.<sup>9</sup> There was no bond greater than 1.574(3) Å in the molecule. 1,1,2,2-Tetracyano-1,2-dihydrotriquinacene has a similar skeleton but with a carbon atom in position 3.<sup>10</sup> In this compound one of the endocyclic bond lengths was long (1.599 Å) and the pentane ring adopted an envelope conformation. In the structure of 7, there are two independent molecules (labelled A and B) in the asymmetric unit. As they are rather different their conformation needs some comments. In A, the cyclobutene ring is planar with deviation from the mean plane of less than 0.006(8) Å and with endocyclic torsion angles less than  $1(1)^\circ$ . The dihedral angles between the four-membered ring and the two methoxycarbonyl substituents

Table 4 Bond angles/ $^\circ$ 

Bond	Angle	Bond	Angle
<b>Compound 6</b>			
C(9)-C(1)-N(2)	111.0(2)	C(10)-C(1)-N(2)	104.5(2)
C(10)-C(1)-C(9)	103.9(2)	C(3)-N(2)-C(1)	106.0(2)
C(13)-N(2)-C(1)	114.1(2)	C(13)-N(2)-C(3)	112.8(2)
C(4)-C(3)-N(2)	103.1(2)	C(5)-C(4)-C(3)	114.8(2)
C(10)-C(4)-C(3)	104.0(2)	C(10)-C(4)-C(5)	102.4(2)
C(6)-C(5)-C(4)	114.6(2)	C(11)-C(5)-C(4)	120.0(2)
C(11)-C(5)-C(6)	125.3(2)	C(7)-C(6)-C(5)	112.1(2)
C(8)-C(7)-C(6)	114.1(2)	C(10)-C(7)-C(6)	102.7(2)
C(10)-C(7)-C(8)	103.8(2)	C(18)-C(7)-C(6)	111.0(2)
C(18)-C(7)-C(8)	111.1(2)	C(18)-C(7)-C(10)	113.8(2)
C(9)-C(8)-C(7)	111.6(2)	C(22)-C(8)-C(7)	124.2(2)
C(22)-C(8)-C(9)	124.2(2)	C(8)-C(9)-C(1)	113.5(2)
C(26)-C(9)-C(1)	118.6(2)	C(26)-C(9)-C(8)	127.2(3)
		C(4)-C(10)-C(1)	105.2(2)
C(7)-C(10)-C(1)	105.1(2)	C(7)-C(10)-C(4)	107.9(2)
C(14)-C(10)-C(1)	110.4(2)	C(14)-C(10)-C(4)	112.5(2)
C(14)-C(10)-C(7)	115.0(2)	N(12)-C(11)-C(5)	176.3(3)
O(15)-C(14)-C(10)	124.9(2)	O(16)-C(14)-C(10)	110.2(2)
O(16)-C(14)-O(15)	124.9(2)	C(17)-O(16)-C(14)	116.3(2)
O(19)-C(18)-C(7)	125.1(2)	O(20)-C(18)-C(7)	109.6(2)
O(20)-C(18)-O(19)	125.3(2)	C(21)-O(20)-C(18)	117.8(3)
O(23)-C(22)-C(8)	124.1(2)	O(24)-C(22)-C(8)	111.6(2)
O(24)-C(22)-O(23)	124.2(2)	C(25)-O(24)-C(22)	115.7(2)
O(27)-C(26)-C(9)	123.3(3)	O(28)-C(26)-C(9)	112.0(3)
O(28)-C(26)-O(27)	124.5(5)	C(29)-O(28)-C(26)	114.3(4)
<b>Compound 7</b>			
	<b>Molecule A</b>	<b>Molecule B</b>	
C(8)-C(1)-C(2)	114.7(4)	112.9(4)	
C(12)-C(1)-C(2)	109.8(4)	111.0(4)	
C(12)-C(1)-C(8)	107.1(4)	107.1(4)	
C(15)-C(1)-C(2)	108.3(4)	108.7(4)	
C(15)-C(1)-C(8)	108.5(4)	108.0(4)	
C(15)-C(1)-C(12)	108.1(4)	109.1(4)	
C(3)-C(2)-C(1)	118.6(4)	117.9(4)	
C(5)-C(2)-C(1)	118.8(4)	116.1(4)	
C(5)-C(2)-C(3)	86.0(3)	85.9(4)	
C(4)-C(3)-C(2)	95.0(4)	94.8(5)	
C(17)-C(3)-C(2)	127.3(4)	128.8(5)	
C(17)-C(3)-C(4)	136.5(4)	136.2(6)	
C(5)-C(4)-C(3)	94.1(4)	93.4(5)	
C(21)-C(4)-C(3)	130.4(5)	134.8(6)	
C(21)-C(4)-C(5)	134.1(5)	131.7(5)	
C(4)-C(5)-C(2)	84.9(4)	85.7(4)	
N(6)-C(5)-C(2)	114.5(4)	113.1(4)	
N(6)-C(5)-C(4)	120.8(4)	119.3(5)	
C(7)-N(6)-C(5)	112.0(4)	106.9(4)	
C(25)-N(6)-C(5)	112.9(4)	110.9(4)	
C(25)-N(6)-C(7)	113.4(5)	110.8(4)	
C(8)-C(7)-N(6)	109.5(4)	110.1(4)	
C(7)-C(8)-C(1)	112.7(4)	112.7(4)	
C(9)-C(8)-C(1)	107.7(4)	108.5(4)	
C(9)-C(8)-C(7)	111.9(4)	113.6(4)	
C(10)-C(9)-C(8)	107.9(4)	108.4(4)	
C(14)-C(9)-C(8)	110.5(4)	109.4(4)	
C(14)-C(9)-C(10)	106.3(5)	105.8(5)	
N(11)-C(10)-C(9)	107.5(4)	108.1(4)	
C(12)-N(11)-C(10)	111.6(4)	111.9(4)	
C(28)-N(11)-C(10)	112.5(5)	112.0(5)	
C(28)-N(11)-C(12)	113.3(5)	113.4(5)	
N(11)-C(12)-C(1)	106.6(4)	105.7(4)	
C(13)-C(12)-C(1)	106.6(4)	107.6(4)	
C(13)-C(12)-N(11)	112.6(4)	111.5(4)	
C(14)-C(13)-C(12)	111.9(5)	112.5(5)	
C(13)-C(14)-C(9)	113.8(5)	114.6(5)	
C(26)-C(14)-C(9)	122.6(6)	120.2(6)	
C(26)-C(14)-C(13)	123.5(5)	125.1(6)	
N(16)-C(15)-C(1)	178.1(6)	177.3(5)	
O(18)-C(17)-C(3)	121.6(5)	122.2(6)	
O(19)-C(17)-C(3)	113.1(5)	111.8(6)	
O(19)-C(17)-O(18)	125.3(5)	126.0(6)	
C(20)-O(19)-C(17)	115.3(4)	116.5(6)	

Table 4 (continued)

Compound 7	Molecule A	Molecule B
O(22)-C(21)-C(4)	124.8(5)	124.9(6)
O(23)-C(21)-C(4)	111.0(5)	113.9(7)
O(23)-C(21)-O(22)	124.1(5)	121.0(7)
C(24)-O(23)-C(21)	116.6(4)	119.4(8)
N(27)-C(26)-C(14)	178.0(6)	178.7(7)

are 45(1) and 15(1)°, respectively for the C(3) and C(4) substituents. On the other hand, the deviations from the least-squares mean plane through the ring atoms [from 0.017(7) to 0.020(8) Å] and the endocyclic torsion angles [ $-3(1)$  to  $+3(1)^\circ$ ] indicate obviously a slight non-planarity for the cyclobutene ring of molecule B. In this case, the dihedral angles between the four-membered ring and the methoxycarbonyl groups are 5(1) and 19(1)°. The conformation of the six-membered C(1)-C(2)-C(5)-N(6)-C(7)-C(8) ring is also different in A and B; the endocyclic torsion angles being 13(1), 0(1),  $-43(1)$ , 73(1),  $-56(1)$ , 13(1) in A compared with 12(1),  $-35(1)$ , 3(1), 51(1),  $-78(1)$  and 43(1) in B. The structure of a polycyclic compound containing the same skeleton as 7 has been published.<sup>11</sup>

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#### References

- H. G. Viehe, Z. Janousek, R. Merényi and L. Stella, *Acc. Chem. Res.*, 1985, **18**, 148.
- F. Liberatore, A. Casini and V. Carelli, *Tetrahedron Lett.*, 1971, **41**, 3829.
- H. Greuter and H. Schmid, *Helv. Chim. Acta*, 1974, **57**, 1204.
- B. De Boeck, B. Bienfait, R. Merényi and H. G. Viehe, Communication at the Belgian Organic Synthesis Symposium 1990, Louvain-la-Neuve.
- G. M. Sheldrick in *Crystallographic Computing 3*, eds. G. M. Sheldrick, C. Kruger and R. Goddard, Oxford University Press, Oxford, 1985, pp. 175-189.
- G. M. Sheldrick, *SHELX 76*. Program for Crystal Structure Determination, University of Cambridge, 1976, England.
- International Tables for X-Ray Crystallography, Vol. IV, Kynoch Press, Birmingham, England, 1974.
- S. Motherwell and W. Clegg, *PLUTO*, University of Cambridge, England, 1978.
- J. B. Hendrickson, *J. Am. Chem. Soc.*, 1964, **86**, 4854.
- L. A. Paquette, S. V. Ley, M. J. Broadhurst, D. Truesdell, J. Fayos and J. Clardy, *Tetrahedron Lett.*, 1973, 2943.
- A. W. Hanson, *Cryst. Struct. Commun.*, 1981, **10**, 319.

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