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## Structure of the Product\* Formed by the Addition of 4-Phenyl-3H-1,2,4-triazole-3,5(4H)-dione to Dimethyl 7H-Benzocycloheptene-7,7-dicarboxylate

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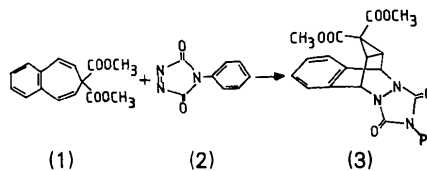
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**Abstract.** C<sub>23</sub>H<sub>19</sub>N<sub>3</sub>O<sub>6</sub>,  $M_r = 433.4$ , monoclinic,  $P2_1/c$ ,  $a = 12.166$  (5),  $b = 13.857$  (5),  $c = 12.331$  (5) Å,  $\beta = 91.84$  (3)°,  $V = 2078$  (2) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.385$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 0.95$  cm<sup>-1</sup>,  $F(000) = 904$ ,  $T = 295$  K,  $R = 0.057$  for 1614 unique observed reflections. The observed bond lengths and bond angles in the cyclopropane ring indicate the presence of a HOMO–LUMO (highest occupied molecular orbital–lowest unoccupied molecular orbital) interaction between the cyclopropane and one methoxycarbonyl group.

**Introduction.** There is much evidence to suggest that cycloheptatriene is in equilibrium with its valence isomer, norcaradiene (Maier, 1967; Kessler, 1972; Balci, 1982). The existence of unsubstituted norcaradiene in equilibrium has been proposed from cycloaddition reactions forming norcaradiene-type adducts. For example, 4-phenyl-1,2,4-triazole-3,5-dione (PTAD) reacts with 7-substituted cycloheptatrienes to give only norcaradiene adducts (Adam, Balci & Pietrzak, 1979). In all cases it has been assumed that dienophiles react with the norcaradiene structure which is in equilibrium. The possibility that norcaradiene adducts can also be formed by a  $(2\pi+2\pi+2\pi)$ -cycloaddition (homo-Diels–Alder addition) has never been considered (Atasoy &

Balci, 1986). To investigate this we synthesized the 7,7-dimethoxycarbonyl-7H-benzocycloheptene (1) which cannot equilibrate with its norcaradiene isomer, and subjected it to PTAD (2). We isolated the title compound (3) in a yield of 30%. The preparation, selected properties and a preliminary report of the structure have been published (Atasoy, Balci & Büyükgüngör, 1987). Here we describe the detailed X-ray analysis of this compound.



**Experimental.** Prepared by the method of Atasoy, Balci & Büyükgüngör (1987), needle-like transparent crystals,  $0.7 \times 0.2 \times 0.02$  mm, Syntex R3 diffractometer, graphite-monochromatized Mo  $K\alpha$ , lattice parameters from setting angles of 18 reflections, intensity data measured by  $\omega$ -scan technique, variable scan speed: max. 12, min.  $2^\circ \text{ min}^{-1}$ , scan range from  $0.9^\circ$  below  $K\alpha_1$  to  $0.9^\circ$  above  $K\alpha_2$ , background/scan ratio 0.5; 3760 reflections measured,  $4.5 \leq 2\theta \leq 43^\circ$ ,  $hkl$  range  $-12, 0, -11$  to  $12, 14, 12$ , 1614 unique reflections considered observed,  $I \geq 3\sigma(I)$ , two check reflections at intervals of 100; variation  $\pm 1.5\%$ ; Lorentz and

\* Dimethyl 10,12-dioxo-11-phenyl-9,11,13-triazapentacyclo-[6.5.3.0<sup>2,7</sup>.0<sup>9,13</sup>.0<sup>14,16</sup>]hexadeca-2(7),3,5-triene-15,15-dicarboxylate.

polarization corrections with *XTAPE* (Sheldrick, 1983), no absorption correction applied. Structure solved by direct methods using *SHELXTL* (Sheldrick, 1983), refinement based on  $|F|$  values carried out with block-cascade algorithm of the same program system, non-H atoms included with anisotropic thermal parameters, all H atoms located from difference Fourier maps and isotropically refined. The results of the refinements are:  $R=0.057$ , unit weights,  $S=1.789$ , normal-probability-slope value 1.313; maximum final shift-to-e.s.d. ratio 0.18, mean 0.037; maximum and minimum heights in final difference Fourier map 0.25 and  $-0.26 e \text{ \AA}^{-3}$ , all calculations performed with *SHELXTL* on a Nova 3 computer, scattering factors taken from *International Tables for X-ray Crystallography* (1974).

**Discussion.** The final atomic coordinates with the equivalent isotropic temperature factors  $U_{eq}$  of the non-H atoms are listed in Table 1, according to the labelling system shown in Fig. 1. The bond lengths are given in Table 2.† The bond lengths within the three-membered ring C(4)–C(5)–C(6) show a tendency not to be equal. The C(4)–C(6) distance, 1.506 (10) Å, is shorter than the C(4)–C(5) and C(5)–C(6) distances which are 1.520 (10) and 1.522 (11) Å respectively. This can be explained on the basis of a HOMO–LUMO (highest occupied molecular orbital–lowest unoccupied molecular orbital) interaction between cyclopropane and the methoxy-carbonyl group (Hoffmann, 1970). Thus it would appear that here also there is a net electron transfer from cyclopropane to the  $\pi$  system. In cyclopropane the C(4)–C(6) bond is antibonding. As a result of the electron transfer from cyclopropane to the  $\pi^*$  orbital of the  $-\text{COOCH}_3$  group, this antibonding diminishes, leading to the stabilization or, in other words, to the shortening of this C(4)–C(6) bond. On the other hand, the interactions between C(4) and C(5), and C(5) and C(6) are bonding. So the electron transfer from cyclopropane to the  $\pi^*$  orbital of the  $-\text{COOCH}_3$  group leads to a longer bond for both C(4)–C(5) and C(5)–C(6) bonds. The C–C distances in the three-membered ring can be compared with those observed for 2,5-dimethyl-7,7-dicyanonorcaradiene (Fritchie, 1966). The close proximity of the methyl group C(81) to the benzene ring could also be observed in the  $^1\text{H}$  NMR spectrum (Atasoy, Balci & Büyükgüngör, 1987). Formation of the norcaradiene adduct supports the view that this product could be formed by the suggested ( $2\pi+2\pi+2\pi$ ) cycloaddition, though a substituent at

C(7) in the cycloheptatriene system like  $-\text{COOCH}_3$  can stabilize the norcaradiene structure. So we cannot distinguish between these two possible mechanisms.

Table 1. Atom coordinates ( $\times 10^4$ ) and equivalent isotropic temperature factors ( $\text{\AA}^2 \times 10^3$ )

Equivalent isotropic  $U$  defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

	x	y	z	$U_{eq}$
O(1)	1142 (3)	6062 (3)	96 (3)	48 (1)
O(2)	3399 (4)	5511 (3)	3094 (3)	56 (2)
O(81)	3313 (3)	1443 (3)	1064 (3)	41 (1)
O(82)	2285 (3)	1672 (3)	-459 (3)	49 (1)
O(92)	76 (4)	1458 (3)	2262 (4)	74 (2)
O(91)	992 (3)	491 (3)	1164 (3)	56 (2)
N(1)	1391 (3)	4738 (3)	1233 (3)	34 (2)
N(2)	2104 (4)	4559 (3)	2174 (3)	36 (2)
N(3)	2254 (4)	6097 (3)	1688 (3)	35 (2)
C(1)	1551 (4)	5684 (4)	895 (5)	34 (2)
C(2)	2690 (5)	5393 (4)	2395 (5)	40 (2)
C(3)	2687 (4)	3608 (4)	2088 (4)	32 (2)
C(4)	1726 (4)	2905 (4)	2088 (4)	32 (2)
C(5)	1551 (4)	2108 (4)	1254 (4)	33 (2)
C(6)	968 (4)	3074 (4)	1117 (4)	33 (2)
C(7)	1397 (4)	3911 (4)	441 (4)	34 (2)
C(8)	2409 (4)	1729 (4)	499 (4)	33 (2)
C(81)	4209 (5)	1087 (5)	419 (5)	57 (2)
C(9)	774 (5)	1323 (4)	1634 (5)	41 (2)
C(91)	284 (6)	-315 (5)	1451 (7)	76 (3)
C(11)	2500 (5)	7106 (4)	1757 (4)	39 (2)
C(12)	2445 (5)	7570 (4)	2741 (4)	46 (2)
C(13)	2726 (6)	8541 (4)	2819 (5)	58 (3)
C(14)	3011 (5)	9047 (4)	1899 (5)	58 (3)
C(15)	3029 (6)	8583 (5)	921 (5)	57 (3)
C(16)	2768 (5)	7610 (4)	834 (5)	47 (2)
C(21)	3290 (4)	3643 (4)	1032 (4)	32 (2)
C(22)	2575 (4)	3801 (4)	139 (4)	32 (2)
C(23)	2999 (5)	3924 (4)	-880 (4)	43 (2)
C(24)	4113 (6)	3895 (5)	-1010 (5)	58 (3)
C(25)	4811 (5)	3752 (5)	-115 (6)	59 (3)
C(26)	4414 (5)	3624 (4)	920 (5)	46 (2)

Table 2. Bond lengths (Å)

O(1)–C(1)	1.208 (9)	O(2)–C(2)	1.211 (9)
O(81)–C(8)	1.342 (9)	O(81)–C(81)	1.456 (10)
O(82)–C(8)	1.189 (8)	O(92)–C(9)	1.183 (10)
O(91)–C(9)	1.322 (10)	O(91)–C(91)	1.4611 (11)
N(1)–N(2)	1.448 (9)	N(1)–C(1)	1.391 (10)
N(1)–C(7)	1.505 (10)	N(2)–C(2)	1.381 (10)
N(2)–C(3)	1.503 (10)	N(3)–C(11)	1.402 (10)
N(3)–C(2)	1.401 (10)	N(3)–C(11)	1.431 (10)
C(3)–C(4)	1.521 (11)	C(3)–C(21)	1.516 (10)
C(4)–C(5)	1.520 (10)	C(4)–C(6)	1.506 (10)
C(5)–C(6)	1.522 (11)	C(5)–C(8)	1.515 (11)
C(5)–C(9)	1.524 (11)	C(6)–C(7)	1.529 (11)
C(7)–C(22)	1.501 (10)	C(11)–C(12)	1.376 (10)
C(11)–C(16)	1.383 (11)	C(12)–C(13)	1.391 (11)
C(13)–C(14)	1.388 (12)	C(14)–C(15)	1.367 (12)
C(15)–C(16)	1.388 (11)	C(21)–C(22)	1.398 (10)
C(21)–C(26)	1.379 (10)	C(22)–C(23)	1.384 (10)
C(23)–C(24)	1.370 (11)	C(24)–C(25)	1.384 (12)
C(25)–C(26)	1.390 (12)		

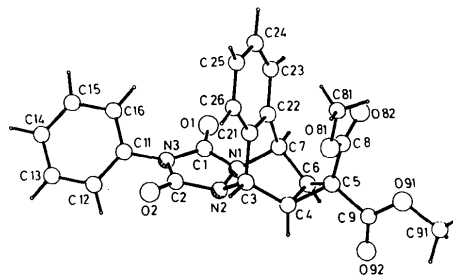


Fig. 1. Perspective view of the molecule with the labelling of the atoms.

† Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and a table of bond angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44534 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## Inside-Protonated 1,7-Diazabicyclo[5.4.3]tetradecane Trifluoromethanesulfonate

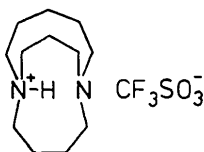
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**Abstract.** C<sub>12</sub>H<sub>25</sub>N<sub>2</sub><sup>+</sup>.CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>, *M<sub>r</sub>* = 346.42, triclinic, *P* $\bar{1}$ , *a* = 12.616 (3), *b* = 7.876 (2), *c* = 8.590 (2) Å,  $\alpha$  = 75.72 (2),  $\beta$  = 85.23 (2),  $\gamma$  = 74.64 (2)°, *V* = 797.5 (4) Å<sup>3</sup>, *Z* = 2, *D<sub>x</sub>* = 1.44 g cm<sup>-3</sup>,  $\lambda$ (Mo *K*α) = 0.71069 Å,  $\mu$  = 2.37 cm<sup>-1</sup>, *F*(000) = 368, *T* = 182 K, *R* = 0.037 for 2904 unique observed reflections. The title compound has an intrabridgehead N(1)··N(7) distance of 2.555 (3) Å; the inside proton is essentially equidistant from both bridgehead nitrogen atoms [N(1)–H 1.293 (25), N(7)–H 1.302 (24) Å].

**Introduction.** The structure analysis of the title compound (1) is one of a series of studies on medium-ring bicyclic diamines and their oxidized and protonated ions (Alder, Orpen & Sessions, 1983; Alder, Orpen & White, 1985, 1988). The interesting physical properties of these compounds are dependent to a large extent on the conformations of the oligomethylene bridges (Alder, 1983), and they also provide a convenient means to study N–H–N hydrogen bonds of various geometries (see Alder *et al.*, 1988).



(1)

**Experimental.** Colourless diamond (0.5 × 0.3 × 0.3 mm) from solvent diffusion using isopropyl alcohol and diethyl ether; Nicolet *P3m* diffractometer, unit cell by least squares based on 23 centred reflections

(12.5 <  $\theta$  < 22.50°), graphite-monochromated Mo *K*α; for data collection 2 <  $\theta$  < 27.50°, temperature 182 K by Nicolet LT-1 N<sub>2</sub> gas flow. Wyckoff  $\omega$  scans, 3645 reflections measured over 60 X-ray hours with no detectable decay or movement. 3448 unique data, *R<sub>merge</sub>* = 0.0121, 2908 reflections with *F* > 3σ(*F*) used for structure solution and refinement (−16 < *h* < 16, 0 < *k* < 11, −12 < *l* < 12). Direct methods and difference-Fourier methods, blocked-cascade least-squares refinement on *F*, *w* = [σ<sup>2</sup>(*F*) + 0.0003(*F*<sup>2</sup>)]<sup>-1</sup>; anisotropic thermal parameters for all non-H atoms, methylene hydrogens were refined in idealized positions (C–H 0.96 Å), all other atoms were refined without constraint. *R* = 0.0374, *wR* = 0.052, *S* = 1.6, data:variable ratio 14.25, max. peak and min. trough in final Δ*F* synthesis 0.43 and 0.21 e Å<sup>-3</sup> respectively, max. shift/e.s.d. in final cycle 0.033; complex neutral-atom scattering factors for C, H, N, O, F, S from *International Tables for X-ray Crystallography* (1974). Computer programs *SHELXTL* (Sheldrick, 1985).

**Discussion.** Atomic coordinates for all non-hydrogen atoms are presented in Table 1,\* selected bond lengths, bond angles, torsion angles and important non-bonded contacts in Table 2; a perspective view of the structure is presented in Fig. 1 and a view of the cation with methylene hydrogens included in Fig. 2. The bicyclic

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44587 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.