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Structure of a 2-Azaspiro[4.5]decadiene

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Abstract. Tetramethyl 3-amino-4-cyano-1-methylene-2-phenyl-2-azaspiro[4.5]deca-3,6-diene-7,8,9,10-tetracarboxylate, $C_{25}H_{25}N_3O_8$, $M_r = 495{\cdot}49$, monoclinic, $C2/c$, $a = 11{\cdot}148\ (5)$, $b = 17{\cdot}156\ (5)$, $c = 26{\cdot}939\ (5)$ Å, $\beta = 93{\cdot}99\ (4)°$, $V = 5139{\cdot}7$ Å^3, $Z = 8$, $D_x = 1{\cdot}281$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}54184$ Å, $\mu = 7{\cdot}724$ cm^{-1}, $F(000) = 2080$, $T = 293$ K. The final R value is 0·071 for 3376 significant $[I > 3\sigma(I)]$ reflections. The title compound is one of the products obtained by thermally or photochemically induced cyclization of the 1:2 adduct of 2-amino-4,5-dimethyl-1-phenylpyrrole-3-carbonitrile and dimethyl acetylenedicarboxylate.

Experimental. The 2-azaspiro[4.5]decadiene crystallizes from chloroform as colorless plates as one of the products of the reaction reported by Eger, Folkers, Frey, Zimmermann & Koop-Kirfel (1988). A single crystal of approximate dimensions 0·10 × 0·40 × 0·40 mm was mounted on a glass fiber. The observed systematic absences determined the space group to be *Cc* or *C*2/*c*, the latter was confirmed by the subsequent refinement. In the final full-matrix least-squares refinement all non-H atoms were assigned anisotropic thermal parameters; the H atomic positions were calculated and included in the structure-factor calculation. However, due to crystal packing effects or disorder, there was no unique way of placing the methyl H atoms of the methoxy groups. The procedure applied to find those positions was to locate the methyl H atoms from a difference Fourier map (using low-angle reflections), which revealed at least one or more H of each group.

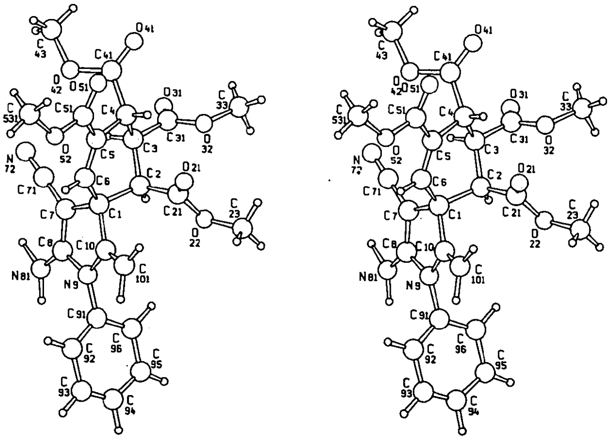

Fig. 1. Stereoview of the molecule with atom labeling using *SCHAKAL* (Keller, 1988).

Table 1. *Data-collection and structure-refinement parameters*

Crystal shape	Plate
Diffractometer used	CAD-4, Enraf–Nonius
Method of intensity measurement	$\theta/2\theta$
No. and θ range of reflections for lattice parameters	25; 9–26°
Method used for absorption correction	*DIFABS* (Walker & Stuart, 1983)
Minimum absorption correction	0·799
Maximum absorption correction	1·375
Average absorption correction	0·933
Maximum value of $(\sin\theta)/\lambda$ reached in intensity measurement (Å^{-1})	0·5877
Range of h, k and l	$0 \rightarrow 13$, $-20 \rightarrow 20$, $-31 \rightarrow 31$
Standard reflections	$0,0,\overline{12}$, $4,0,10$, $0,6,\overline{12}$
Interval, standard reflections measured	2h, no intensity variation
Total No. of reflections measured; θ range (°)	7853; 65 (1347 unobserved reflections)
No. of observed unique reflections	3376 with $I > 3\sigma(I)$
Methods used to solve structure	Direct methods (*SHELXS*; Sheldrick, 1985)
Use of F or F^2 in LS refinement	F
Method of locating H atoms	H positions calculated in idealized positions
Weighting scheme	$1/\sigma^2$
Parameters refined	335
Value of R	0·071
Value of wR	0·066
Ratio of max. LS shift to e.s.d. (Δ/σ)	0·001
Max. height in final ΔF map (e Å^{-3})	0·322
Error in an observation of unit weight	2·776
Secondary extinction coefficient	$9{\cdot}417(1) \times 10^{-7}$ (Zachariasen, 1963)
Sources of atomic scattering factors	*International Tables for X-ray Crystallography* (1974)
Computer used	MicroVAX 3500
Programs used	*VAXSDP* version 3.0 (1986) (Frenz, 1978)

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Table 2. *Positional parameters and equivalent isotropic thermal parameters U_{eq} (Å^2)*

The atoms C531 and C532 have each been refined with multiplicity 0·5.

$$U_{\rm eq} = (U_{11} + U_{22} + U_{33})/3.$$

	x	y	z	$U_{\rm eq}$
O21	0·0991 (2)	0·4966 (2)	0·17490 (9)	0·057 (2)
O22	−0·0257 (3)	0·4219 (2)	0·1281 (1)	0·103 (3)
O31	0·1354 (3)	0·5438 (2)	0·0002 (1)	0·077 (2)
O32	0·1905 (4)	0·4788 (2)	0·0678 (1)	0·116 (3)
O41	0·3506 (3)	0·6617 (2)	0·0736 (1)	0·083 (3)
O42	0·2109 (3)	0·7535 (2)	0·0798 (1)	0·070 (2)
O51	0·2997 (3)	0·7224 (2)	0·1892 (1)	0·089 (2)
O52	0·1335 (4)	0·7665 (2)	0·2195 (1)	0·126 (3)
N9	−0·2954 (3)	0·5872 (2)	0·1364 (1)	0·055 (2)
N72	−0·1072 (3)	0·7594 (2)	0·0299 (2)	0·073 (3)
N81	−0·3867 (3)	0·6569 (2)	0·0687 (1)	0·060 (2)
C1	−0·0902 (3)	0·6172 (2)	0·1320 (1)	0·043 (2)
C2	−0·0198 (3)	0·5533 (2)	0·1049 (1)	0·040 (2)
C3	0·0826 (3)	0·5930 (2)	0·0784 (1)	0·037 (2)
C4	0·1756 (3)	0·6317 (2)	0·1164 (1)	0·040 (2)
C5	0·1124 (3)	0·6759 (2)	0·1556 (1)	0·044 (2)
C6	−0·0042 (3)	0·6692 (2)	0·1621 (1)	0·050 (2)
C7	−0·1716 (3)	0·6630 (2)	0·0949 (1)	0·045 (2)
C8	−0·2883 (3)	0·6388 (2)	0·0975 (1)	0·048 (2)
C10	−0·1836 (3)	0·5802 (3)	0·1630 (1)	0·053 (3)
C21	0·0276 (4)	0·4897 (2)	0·1404 (2)	0·052 (2)
C23	0·0158 (7)	0·3557 (3)	0·1581 (3)	0·196 (6)
C31	0·1404 (3)	0·5378 (2)	0·0438 (1)	0·047 (2)
C33	0·2459 (8)	0·4216 (4)	0·0370 (3)	0·209 (7)
C41	0·2581 (3)	0·6829 (2)	0·0883 (1)	0·050 (2)
C43	0·2802 (6)	0·8092 (3)	0·0534 (2)	0·103 (4)
C51	0·1917 (4)	0·7239 (3)	0·1890 (2)	0·071 (3)
C531	0·192 (1)	0·8349 (7)	0·2438 (5)	0·13 (1)
C532	0·222 (1)	0·7916 (7)	0·2642 (5)	0·14 (1)
C71	−0·1357 (3)	0·7163 (2)	0·0595 (2)	0·049 (2)
C91	−0·3972 (4)	0·5415 (3)	0·1459 (2)	0·065 (3)
C92	−0·4835 (4)	0·5694 (4)	0·1737 (2)	0·101 (5)
C93	−0·5837 (5)	0·5248 (5)	0·1828 (2)	0·181 (8)
C94	−0·5866 (7)	0·4555 (5)	0·1637 (4)	0·199 (8)
C95	−0·5048 (8)	0·4232 (5)	0·1349 (5)	0·24 (2)
C96	−0·4060 (6)	0·4689 (4)	0·1278 (3)	0·144 (9)
C101	−0·1675 (4)	0·5483 (4)	0·2076 (2)	0·084 (4)

In a succeeding step we placed the other missing H atoms by idealized geometry.

One methyl group occupies split positions (C531, C532), each refined with population 0·5. In the stereoview of Fig. 1 only the position C531 is displayed for clarity.

More details of the intensity-data collection, structure solution and refinement are listed in Table 1. Final atomic coordinates are given in Table 2, distances and angles in Table 3.*

Related literature. As part of our studies on the synthesis of biologically active heterocyclic spiro compounds we recently described the formation of a Michael adduct of ascorbic acid with acrolein (Eger, Folkers, Zimmermann, Schmidt & Hiller, 1987).

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Table 3. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s*

O21	C21	1·188 (5)
O22	C21	1·338 (5)
O22	C23	1·453 (8)
O33	C31	1·178 (5)
O32	C31	1·307 (6)
O32	C33	1·450 (8)
O41	C41	1·187 (5)
O42	C41	1·334 (5)
O42	C43	1·447 (6)
O51	C51	1·204 (6)
O52	C51	1·306 (6)
O52	C531	1·47 (1)
O52	C532	1·57 (1)
N9	C8	1·378 (6)
N9	C10	1·400 (5)
N9	C91	1·418 (5)
N72	C71	1·147 (6)
N81	C8	1·336 (5)
C1	C2	1·559 (6)
C1	C6	1·506 (5)
C1	C7	1·521 (5)
C1	C10	1·520 (5)
C2	C3	1·546 (5)
C2	C21	1·521 (5)
C3	C4	1·555 (5)
C3	C31	1·505 (5)
C4	C5	1·513 (6)
C4	C41	1·513 (5)
C5	C6	1·329 (5)
C5	C51	1·468 (6)
C7	C8	1·372 (5)
C7	C71	1·399 (5)
C10	C101	1·320 (7)
C91	C92	1·347 (7)
C91	C96	1·338 (8)
C92	C93	1·390 (9)
C93	C94	1·30 (1)
C94	C95	1·36 (1)
C95	C96	1·38 (1)
C531	C532	0·97 (2)

C21	O22	C23	115·0 (4)
C31	O32	C33	115·3 (4)
C41	O42	C43	117·8 (4)
C51	O52	C531	120·1 (7)
C51	O52	C532	108·8 (6)
C8	N9	C10	110·4 (3)
C8	N9	C91	125·7 (3)
C10	N9	C91	123·7 (3)
C2	C1	C6	110·3 (3)
C2	C1	C7	110·7 (3)
C2	C1	C10	110·5 (3)
C6	C1	C7	112·2 (3)
C6	C1	C10	112·7 (3)
C7	C1	C10	100·3 (3)
C1	C2	C3	108·6 (3)
C1	C2	C21	112·0 (3)
C3	C2	C21	111·8 (3)
C2	C3	C4	111·5 (3)
C2	C3	C31	111·7 (3)
C4	C3	C31	112·5 (3)
C3	C4	C5	110·6 (3)
C3	C4	C41	108·7 (3)
C5	C4	C41	112·8 (4)
C4	C5	C6	123·7 (3)
N9	C91	C92	121·1 (4)
N9	C91	C96	119·1 (5)
C92	C91	C96	119·9 (5)
C91	C92	C93	121·0 (6)
C92	C93	C94	115·7 (6)
C4	C5	C51	114·8 (3)
C6	C5	C51	121·4 (4)
C1	C6	C5	125·1 (3)
C1	C7	C8	109·5 (3)
C1	C7	C71	126·9 (3)
C8	C7	C71	123·4 (3)
N9	C8	N81	120·2 (3)
N9	C8	C7	109·8 (3)
N81	C8	C7	129·9 (4)
N9	C10	C1	107·5 (4)
N9	C10	C101	124·3 (4)
C1	C10	C101	128·3 (4)
O21	C21	O22	122·9 (4)
O21	C21	C2	127·4 (4)
O22	C21	C2	109·8 (3)
O31	C31	O32	123·4 (4)
O31	C31	C3	124·8 (4)
O32	C31	C3	111·6 (3)
O41	C41	O42	124·3 (4)
O41	C41	C4	124·2 (4)
O42	C41	C4	111·5 (3)
O51	C51	O52	123·3 (4)
O51	C51	C5	123·4 (4)
O52	C51	C5	113·3 (4)
N72	C71	C7	178·9 (4)
C93	C94	C95	127·1 (8)
C94	C95	C96	115·0 (8)
C91	C96	C95	121·3 (7)

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* Lists of structure factors, H positions, torsional angles and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52200 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of 4-Oxo-5,6,7,8-tetrahydro-3*H*-cyclohexathieno[2,3-*d*]pyrimidine

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Abstract. $C_{10}H_{10}N_2OS$, $M_r = 206{\cdot}3$, monoclinic, $P2_1/n$, $a = 6{\cdot}943\,(2)$, $b = 13{\cdot}216\,(2)$, $c = 10{\cdot}342\,(2)$ Å, $\beta = 101{\cdot}1\,(2)°$, $V = 931{\cdot}2$ Å^3, $Z = 4$, $D_x = 1{\cdot}47$ g cm^{-3}, $\lambda(\mathrm{Cu}\,K\alpha) = 1{\cdot}5418$ Å, $\mu = 7{\cdot}5$ cm^{-1}, $F(000) = 432$, $T = 296$ K, $R = 0{\cdot}06$ for 1610 observed reflections. Molecular geometry is normal. The thiophene ring is planar, and is coplanar with the 3*H*-pyrimidinone ring [dihedral angle = 0·7 (1)°]. The fused cyclohexene ring adopts a half-chair conformation. The C—S distances are 1·726 (3) and 1·738 (3) Å. The C—S—C bond angle is 91·6 (1)°.

Experimental. 2-Aminothiophenes were prepared by adopting the following procedure: a cycloalkanone was allowed to undergo a Cope reaction (Cope, Hofmann, Wyckoff & Hardenbergh, 1941), followed by a Gewald reaction in the presence of sulfur, to form substituted cycloalka[*b*]thiophenes (Gewald, 1962, 1965; Gewald, Schinke & Bottcher, 1966). 2-Amino-3-(ethoxycarbonyl)-4,5,6,7-tetrahydrocyclohexa[*b*]thiophene was dissolved in formamide. The mixture was boiled under reflux at 473 K for 18 h. On cooling to room temperature a crystalline precipitate was obtained, which was filtered, washed with 2-propanol, and recrystallized from chloroform–methanol–propanol. The 4-oxo-5,6,7,8-tetrahydro-3*H*-cyclohexathieno[2,3-*d*]pyrimidine was obtained as light brown needles.

A specimen of dimensions 0·29 × 0·20 × 0·25 mm was chosen. Lattice parameters and their e.s.d.'s derived from a least-squares treatment of 25 reflections ($25 < \theta < 35°$). Intensity data were collected on an Enraf–Nonius CAD-4 single-crystal X-ray diffractometer, graphite-crystal-monochromated Cu $K\alpha$ radiation, $\omega/2\theta$ scan mode for h $0\rightarrow 8$, k $-8\rightarrow 14$, l $-12\rightarrow 12$, $2\theta_{\max} = 140°$. Two standard reflections monitored every 100 measurements varied less than 2%. Of the 2052 independent reflections collected 1610 were judged significant [$I > 3\sigma(I)$]. $R_{\mathrm{int}} = 0{\cdot}01$. Intensities were corrected for Lp effects, absorption corrections were ignored. Structure solved by Patterson methods using *SHELXS*86 (Sheldrick, 1986). Positional and thermal parameters of non-hydrogen

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters for non-hydrogen atoms, with e.s.d.'s in parentheses*

$$B_{\mathrm{eq}} = \tfrac{8}{3}\pi^2\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}(Å^2)
S(1)	0·1758 (1)	0·1089 (1)	0·2659 (1)	4·0
C(2)	−0·0235 (3)	0·0500 (2)	0·3105 (2)	3·0 (1)
N(3)	−0·0859 (3)	−0·0437 (2)	0·2652 (2)	3·5
C(4)	−0·2348 (4)	−0·0757 (2)	0·3106 (2)	3·4 (1)
N(5)	−0·3282 (3)	−0·0235 (2)	0·3939 (2)	2·5
C(6)	−0·2721 (3)	0·0725 (2)	0·4428 (2)	3·0 (1)
C(7)	−0·1053 (3)	0·1105 (2)	0·3956 (2)	2·8 (1)
C(8)	−0·0040 (3)	0·2048 (2)	0·4257 (2)	3·0 (1)
C(9)	−0·0500 (4)	0·2849 (2)	0·5174 (2)	3·7 (1)
C(10)	0·1209 (6)	0·3561 (3)	0·5599 (4)	5·3 (1)
C(11)	0·2126 (6)	0·3894 (2)	0·4459 (4)	5·4 (1)
C(12)	0·2906 (5)	0·3002 (2)	0·3746 (3)	4·7 (1)
C(13)	0·1498 (4)	0·2138 (2)	0·3625 (2)	3·5 (1)
O(14)	−0·3629 (3)	0·1144 (1)	0·5177 (2)	3·8

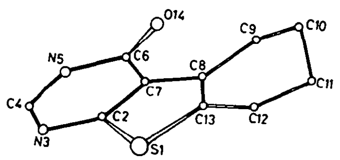

Fig. 1. Perspective view of the molecule showing atomic nomenclature.

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