

Table 1. *Positional and equivalent isotropic thermal parameters for the non-H atoms with e.s.d.'s in parentheses*

	$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$			
	x	y	z	$U_{eq}(\text{\AA}^2)$
N(1)	0.1627 (1)	0.1730 (1)	0.3118 (1)	0.0587 (6)
N(2)	0.0451 (2)	0.0752 (1)	0.5637 (1)	0.0653 (6)
Li	0.0832 (3)	0.25	0.25	0.055 (2)
C(1)	0	0.25	0.3758 (2)	0.047 (1)
C(2)	0.0430 (1)	0.1984 (1)	0.4272 (1)	0.0470 (6)
C(3)	0.0434 (1)	0.1973 (1)	0.5220 (2)	0.0520 (6)
C(4)	0	0.25	0.5676 (2)	0.056 (1)
C(5)	0.0926 (2)	0.1435 (1)	0.3731 (1)	0.0560 (6)
C(6)	0.2390 (2)	0.2016 (1)	0.3651 (2)	0.089 (1)
C(7)	0.1982 (2)	0.1200 (1)	0.2516 (2)	0.098 (1)
C(8)	0.0886 (2)	0.1414 (1)	0.5765 (2)	0.065 (1)
C(9)	-0.0506 (2)	0.0756 (1)	0.5939 (2)	0.094 (1)
C(10)	0.0977 (2)	0.0230 (1)	0.6102 (2)	0.102 (1)

A view of the molecule with the adopted atom numbering is shown in Fig. 1. Final atomic parameters are given in Table 1,\* bond distances and angles in Table 2.

**Related literature.** For the preparation of the title compound and a discussion of the results see van der Zeijden, van Koten, Smeets & Spek (1987). The present structure resembles that of other two-electron three-centre-bonded aryllithium compounds like Li<sub>2</sub>Ph<sub>2</sub>-(TMEDA)<sub>2</sub> (Thoennes & Weiss, 1978); Li<sub>2</sub>[8-(dimethylamino)-1-naphthyl]<sub>2</sub>(Et<sub>2</sub>O)<sub>2</sub> (Jastrzebski, van Koten, Goubitz, Arlen & Pfeffer, 1983) and Li<sub>2</sub>(mesityl)<sub>2</sub>(THF)<sub>4</sub> (Beno, Hope, Olmstead & Power, 1985).

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\* Lists of structure factors, anisotropic thermal parameters and geometrical data for H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43806 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond distances (Å) and bond angles (°) for the non-H atoms with e.s.d.'s in parentheses*

N(1)—C(5)	1.476 (3)	Li—C(1)	2.209 (3)
N(1)—C(6)	1.465 (3)	C(1)—C(2)	1.411 (2)
N(1)—C(7)	1.463 (3)	C(2)—C(5)	1.522 (3)
N(1)—Li	2.109 (3)	C(2)—C(3)	1.397 (3)
N(2)—C(8)	1.459 (3)	C(3)—C(8)	1.511 (3)
N(2)—C(10)	1.450 (3)	C(3)—C(4)	1.386 (3)
N(2)—C(9)	1.451 (4)		
Li—N(1)—C(5)	100.1 (2)	Li—C(1)—Li <sup>i</sup>	65.9 (2)
Li—N(1)—C(6)	111.3 (2)	Li—C(1)—C(2)	102.2 (1)
Li—N(1)—C(7)	116.2 (1)	Li—C(1)—C(2)	133.6 (1)
C(5)—N(1)—C(6)	109.8 (2)	C(2)—C(1)—C(2)	115.1 (2)
C(5)—N(1)—C(7)	109.3 (2)	C(3)—C(2)—C(5)	120.7 (2)
C(6)—N(1)—C(7)	109.7 (2)	C(1)—C(2)—C(5)	115.9 (2)
C(8)—N(2)—C(9)	111.4 (2)	C(1)—C(2)—C(3)	123.3 (2)
C(8)—N(2)—C(10)	110.3 (2)	C(2)—C(3)—C(8)	123.0 (2)
C(9)—N(2)—C(10)	110.9 (2)	C(4)—C(3)—C(8)	118.9 (3)
N(1)—Li—C(1)	86.17 (5)	C(2)—C(3)—C(4)	118.1 (2)
N(1)—Li—N(1 <sup>ii</sup> )	114.1 (2)	C(3)—C(4)—C(3)	122.0 (3)
N(1)—Li—C(1 <sup>ii</sup> )	131.17 (5)	N(1)—C(5)—C(2)	111.3 (2)
C(1)—Li—C(1 <sup>ii</sup> )	114.1 (2)	N(2)—C(8)—C(3)	113.4 (2)

Symmetry code: (i)  $-x, \frac{1}{2}-y, z$ ; (ii)  $x, \frac{1}{2}-y, \frac{1}{2}-z$ .

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## Structure of 2,6-Dimethyl-4-phenyl-4H-pyran-3,5-dicarbonitrile

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**Abstract.** C<sub>15</sub>H<sub>12</sub>N<sub>2</sub>O,  $M_r = 236.273$ , orthorhombic, *Pbca*,  $a = 22.866$  (2),  $b = 13.173$  (1),  $c = 8.517$  (1) Å,  $V = 2565.3$  (2) Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 1.2235$  g cm<sup>-3</sup>,

$\lambda(\text{Mo K}\alpha) = 0.7107$  Å,  $\mu = 0.732$  cm<sup>-1</sup>,  $F(000) = 992$ , room temperature,  $R = 0.060$ ,  $wR = 0.038$  for 1261 observed reflections. The pyran ring has approximate *m*

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Table 1. Atomic parameters and their *e.s.d.*'s
$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j \cos(\mathbf{a}_i, \mathbf{a}_j).$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub> (Å <sup>2</sup> × 10 <sup>3</sup> )
O1	0.1123 (1)	0.2335 (2)	0.0352 (3)	57 (1)
C2	0.1640 (2)	0.2162 (3)	−0.0444 (5)	55 (2)
C3	0.1824 (2)	0.1231 (3)	−0.0785 (5)	48 (2)
C4	0.1496 (2)	0.0265 (3)	−0.0374 (5)	45 (1)
C5	0.0972 (2)	0.0567 (3)	0.0602 (4)	42 (1)
C6	0.0800 (2)	0.1512 (3)	0.0895 (5)	48 (1)
C7	0.1918 (3)	0.3158 (4)	−0.0877 (8)	74 (3)
C8	0.2364 (2)	0.1123 (4)	−0.1628 (6)	63 (2)
N9	0.2788 (2)	0.0989 (3)	−0.2300 (5)	91 (2)
C10	0.1322 (2)	−0.0302 (3)	−0.1847 (5)	42 (1)
C11	0.1009 (2)	0.0162 (3)	−0.3030 (5)	53 (2)
C12	0.0850 (2)	−0.0341 (4)	−0.4381 (6)	58 (2)
C13	0.1003 (2)	−0.1357 (4)	−0.4552 (6)	66 (2)
C14	0.1304 (2)	−0.1844 (4)	−0.3383 (7)	70 (2)
C15	0.1466 (2)	−0.1317 (3)	−0.2034 (5)	49 (2)
C16	0.0622 (2)	−0.0267 (3)	0.1186 (5)	48 (2)
N17	0.0357 (2)	−0.0935 (3)	0.1624 (5)	68 (2)
C18	0.0278 (2)	0.1861 (4)	0.1767 (8)	65 (2)

symmetry extended to the two methyl and the two cyano groups. Only the torsion angle around the bond between the phenyl and the pyran rings, of 60.0 (2)°, breaks this *m* symmetry in the molecule. The dihedral angle between the two rings is 94.1 (1)°. The pyran ring displays a very flattened boat conformation.

**Experimental.** Title compound provided by Drs N. Martin and C. Seoane of the Universidad of Madrid. Crystal of dimensions 0.20 × 0.23 × 0.27 mm selected for X-ray analysis. Nonius CAD-4 diffractometer, graphite monochromator, accurate unit-cell parameters from least-squares refinement on 25 reflections, with  $\theta_{\max} = 22^\circ$ . Intensity data were collected on the same diffractometer with Mo *K*α radiation, using the  $\omega$ -2 $\theta$  scan technique in the range  $2 < \theta < 30^\circ$ ,  $0 < h < 12$ ,  $0 < k < 13$ ,  $0 < l < 10$ . Two reflections (302 and  $\bar{3}0\bar{2}$ ) were used as standard and remeasured after 100 reflections, no decomposition was observed. Of the 2182 reflections measured, only 1261 unique reflections were considered as observed with  $I > 2\sigma(I)$ ,  $\sigma$  being determined from counting statistics. Lorentz and polarization corrections applied, absorption ignored.

The structure was solved by direct methods with *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and Fourier synthesis. The refinement of the structure was carried out by full-matrix least squares with anisotropic temperature factors for all non-H atoms and isotropic temperature factors for all H atoms located in a  $\Delta F$  map.  $R = 0.060$  and  $wR = 0.038$  with  $w$  calculated using an empirical weighting scheme fitted so as to give no trends in  $\langle w\Delta F \rangle$  vs  $\langle \sin \theta / \lambda \rangle$ ;  $S = 0.90$ , max.  $\Delta/\sigma = 0.02$ , max. height in final  $\Delta F$  synthesis 0.20, min. =  $-0.35 \text{ e } \text{\AA}^{-3}$ . Asymmetry parameters of the pyran ring are  $\Delta C_s(\text{O1}) = 0.008$  (2),  $\Delta C_s(\text{C2}-\text{C3}) = 0.011$  (2) in terms of Nardelli (1983b).

Table 2. Bond distances (Å), bond angles (°) and torsion angles (°)

O1—C2	1.380 (5)	O1—C6	1.391 (5)
C2—C3	1.330 (6)	C2—C7	1.503 (7)
C3—C4	1.518 (6)	C3—C8	1.435 (6)
C4—C5	1.511 (5)	C4—C10	1.513 (6)
C5—C6	1.330 (6)	C5—C16	1.447 (6)
C6—C18	1.479 (7)	C8—N9	1.138 (6)
C10—C11	1.378 (6)	C10—C15	1.387 (6)
C11—C12	1.377 (7)	C12—C13	1.391 (7)
C13—C14	1.370 (8)	C14—C15	1.392 (7)
C16—N17	1.132 (6)		
C2—O1—C6	119.3 (3)	O1—C2—C7	109.8 (4)
O1—C2—C3	122.1 (4)	C3—C2—C7	128.1 (4)
C2—C3—C8	118.3 (4)	C2—C3—C4	124.4 (4)
C4—C3—C8	117.3 (4)	C3—C4—C10	110.7 (3)
C3—C4—C5	107.4 (3)	C5—C4—C10	112.2 (3)
C4—C5—C16	115.3 (3)	C4—C5—C6	125.8 (4)
C6—C5—C16	118.9 (4)	O1—C6—C5	120.6 (3)
C5—C6—C18	128.6 (4)	O1—C6—C18	110.7 (4)
C3—C8—N9	176.7 (5)	C4—C10—C15	120.6 (4)
C4—C10—C11	121.6 (4)	C11—C10—C15	117.8 (4)
C10—C11—C12	122.4 (4)	C11—C12—C13	118.9 (4)
C12—C13—C14	120.0 (5)	C13—C14—C15	120.0 (5)
C10—C15—C14	120.8 (4)	C5—C16—N17	178.4 (5)
C2—O1—C6—C5	177.7 (4)	C2—O1—C6—C18	−2.6 (5)
C6—O1—C2—C3	−178.6 (4)	C6—O1—C2—C7	3.7 (6)
O1—C2—C3—C4	0.9 (7)	O1—C2—C3—C8	179.5 (4)
C7—C2—C3—C8	2.2 (7)	C7—C2—C3—C4	−176.4 (5)
C2—C3—C4—C5	−5.4 (6)	C2—C3—C4—C10	117.3 (5)
C8—C3—C4—C10	−61.3 (5)	C8—C3—C4—C5	175.9 (4)
C3—C4—C10—C11	−54.1 (5)	C3—C4—C10—C15	127.0 (4)
C3—C4—C5—C6	6.6 (5)	C3—C4—C5—C16	−176.5 (3)
C5—C4—C10—C11	65.8 (5)	C5—C4—C10—C15	−113.1 (4)
C10—C4—C5—C16	61.7 (5)	C10—C4—C5—C6	−115.2 (4)
C4—C5—C6—O1	−3.1 (6)	C4—C5—C6—C18	176.5 (4)
C16—C5—C6—O1	−179.9 (3)	C16—C5—C6—C18	−0.3 (7)

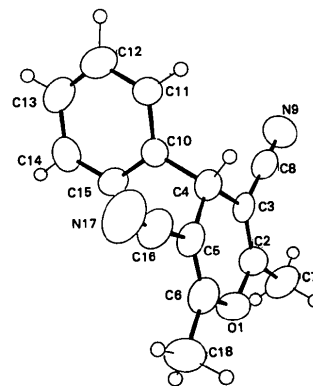


Fig. 1. A view of the molecule with the atomic labelling.

The computations were made with *XRAY*76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976), *PARST* (Nardelli, 1983a) and *PESOS* (Martinez-Ripoll & Cano, 1975) on a VAX11/750 computer. The anomalous-scattering coefficients and scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Table 1 shows the

atomic coordinates,\* Table 2 displays the bond lengths and angles, and Fig. 1 shows a view of the molecule with the numbering used in the crystallographic study.

**Related literature.** Structure of 2-[*o*-(methylthio)benzylideneamino]-2-phenyl-1,1-ethylenedicarbonitrile (Balcazar, Florencio & García-Blanco, 1985) and tandem [2,3]sigmatropic rearrangement of a sulfonium ylide and cyclopropanation of the resulting electron-rich olefin on a 4-methoxy-2-pyrone derivative (de March, Moreno-Manas, Ripoll, Florencio, García-Blanco & Martínez-Carrera, 1986).

\* 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 43778 (18 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 2-Methylthio-2-[ $\alpha$ -(methylthio)ethylideneamino]-1,1-ethylenedicarbonitrile

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(Received 28 August 1986; accepted 2 February 1987)

**Abstract.**  $C_8H_9N_3S_2$ ,  $M_r = 211.30$ , triclinic,  $P\bar{1}$ ,  $a = 10.489$  (4),  $b = 14.230$  (9),  $c = 7.790$  (4) Å,  $\alpha = 94.74$  (1),  $\beta = 110.36$  (1),  $\gamma = 86.34$  (1)°,  $V = 1085.6$  (9) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.293$  g cm<sup>-3</sup>, Mo  $K\alpha$ ,  $\lambda = 0.7107$  Å,  $\mu = 4.315$  cm<sup>-1</sup>,  $F(000) = 440$ , room temperature, final  $R = 0.054$  and  $wR = 0.069$  for 5174 observed reflections. The configuration at the C=N bond is (*E*). The C–C(CN)<sub>2</sub> groups are nearly planar. The torsion angles C=N–C=C are 80.6 (3) and –84.1 (3)° respectively on the two independent molecules.

**Experimental.** Crystal 0.40 × 0.35 × 0.50 mm. Enraf–Nonius CAD-4 automatic diffractometer, 25 reflections used in determination of lattice parameters ( $8 < \theta < 13^\circ$ ), absorption correction (transmission factors 0.62–1.36). Data collection: Mo  $K\alpha$ ,  $2 < \theta < 30^\circ$ ,  $h = -14$  to 14,  $k = 0$  to 14,  $l = -10$  to 10. Two check reflections ( $\bar{2}15$ ,  $10\bar{7}$ ) measured every 100 reflections showed no significant variation; 6166 unique reflections measured, 5174 observed with  $I > 2\sigma(I)$ .  $R_{int} = 0.085$ . Structure solved by direct methods with *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson,

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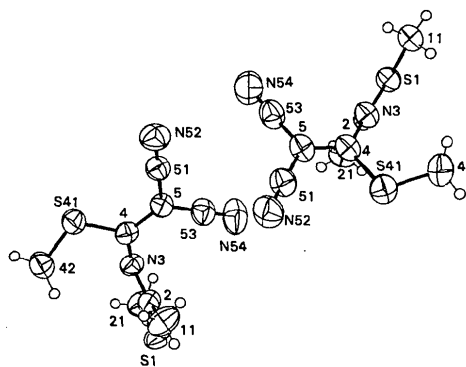


Fig. 1. A view of the molecule with the atomic labelling.

1980); refined by full-matrix least squares with  $\sum w(|F_o| - |F_c|)^2$  minimized; unit weights since an applied weighting scheme (Martínez-Ripoll & Cano, 1975) gave no trends in  $F_o$  and  $\sin \theta/\lambda$ ; anisotropic thermal parameters for non-H atoms.

All H atoms located in difference Fourier synthesis, positional parameters included in further refinement