

Structure of {2,3,5,6-Tetrakis[(dimethylamino)methyl]phenyl-C,N,N'}lithium Dimer

By W. J. J. SMEETS AND A. L. SPEK*

Vakgroep Algemene Chemie, Afdeling Kristal- en Structuurchemie, University of Utrecht, Padualaan 8, 3508 TB Utrecht, The Netherlands

AND A. A. H. VAN DER ZEIJDEN AND G. VAN KOTEN

Anorganisch Chemisch Laboratorium, University of Amsterdam, 1018 WV Amsterdam, The Netherlands

(Received 22 January 1987; accepted 23 February 1987)

Abstract. $C_{36}H_{66}Li_2N_8$, $Li_2(C_{18}H_{33}N_4)_2$, $M_r = 624.85$, orthorhombic, $Ccca$, $a = 14.432$ (3), $b = 19.697$ (2), $c = 14.739$ (1) Å, $V = 4190$ (1) Å³, $Z = 4$, $D_x = 0.990$ g cm⁻³, $Mo K\alpha$, $\lambda = 0.71073$ Å, $\mu = 0.6$ cm⁻¹, $F(000) = 1376$, $T = 294$ K, $R = 0.0550$ for 1256 observed reflections with $I > 2\sigma(I)$. The crystal structure consists of four dimeric molecules in the orthorhombic unit cell with no significant short intermolecular contact; the molecules have crystallographic 222 site symmetry. The Li atom is pseudo-tetrahedrally coordinated by two N(1) atoms [2.109 (3) Å] and by two C(1) atoms [2.209 (3) Å].

Experimental. Colourless rod-shaped crystal $1.0 \times 0.33 \times 0.33$ mm mounted under nitrogen in a Lindemann-glass capillary. Unit-cell parameters and their e.s.d.'s derived from a least-squares treatment of 12 reflections ($9.3 < \theta < 11.2^\circ$). 2407 intensity data were collected within one octant of the reflection sphere ($0 \leq h \leq 18$; $0 \leq k \leq 25$; $0 \leq l \leq 19$; $1.38 < \theta < 27.5^\circ$) on an Enraf–Nonius CAD-4F diffractometer, Zr-filtered $Mo K\alpha$ radiation, $\omega/2\theta$ scan mode with $\Delta\omega = (0.60 + 0.35 \tan \theta)^\circ$. Three reference reflections (400, 040, 004) measured every hour of X-ray exposure time showed a small linear decay of 1.2%. Intensity data were corrected for this decay and for Lorentz–polarization effects. Standard deviations of the intensities were increased according to an analysis of the excess variance of the reference reflections: $\sigma^2(I) = \sigma_{cs}^2(I) + (0.013I)^2$ resulting in 1256 observed reflections with $I > 2\sigma(I)$ (McCandlish, Stout & Andrews, 1975). Space group $Ccca$ derived from the systematic absences: hkl : $h+k=2n+1$; $0kl$: $k, l=2n+1$; $h0l$: $h, l=2n+1$; $hk0$: $h, k=2n+1$. Structure solved by direct methods (*SHELXS86*; Sheldrick, 1986), the solution with the best figure of merit revealed all non-H atoms with the exception of Li. The position of the Li atom was determined from a subsequent difference Fourier synthesis. All non-H atoms refined with anisotropic thermal parameters by full-matrix least-

squares techniques, minimizing $\sum w\Delta F^2$, using the *SHELX76* package (Sheldrick, 1976). All H atoms except H(4) were introduced on calculated positions ($C-H=0.98$ Å) and refined riding on their corresponding C atoms, with one overall isotropic thermal parameter. H(4) was located from a difference Fourier synthesis and refined according to its special position with the same isotropic thermal parameter. At the final stage of the refinement, weights were introduced resulting in $R = 0.0550$, $wR = 0.0405$, $S = 2.64$, $w = 1/\sigma^2(F)$. Max. $\Delta/\sigma = 0.17$. A final difference Fourier map revealed residual densities between 0.18 and -0.16 e Å⁻³. The crystal exhibited some secondary extinction for which the F_c values were corrected by refinement of an empirical isotropic extinction parameter $X[=3.0(6) \times 10^{-8}]$: $F'_c = F_c[1 - (XF^2/\sin \theta)]$. Scattering factors were taken from Cromer & Mann (1968). All calculations were carried out in the CDC Cyber-855 of the University of Utrecht Computer Center with the programs mentioned above and with the *EUCLID* package (Spek, 1982; molecular geometry and illustrations).

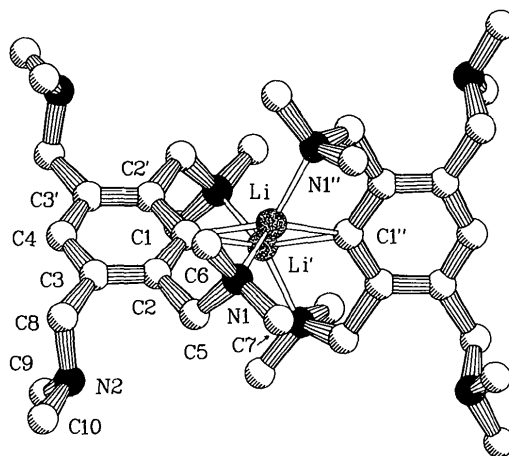


Table 1. *Positional and equivalent isotropic thermal parameters for the non-H atoms with e.s.d.'s in parentheses*

	$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$			
	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 Li₂Ph₂-(TMEDA)₂ (Thoennes & Weiss, 1978); Li₂[8-(dimethylamino)-1-naphthyl]₂(Et₂O)₂ (Jastrzebski, van Koten, Goubitz, Arlen & Pfeffer, 1983) and Li₂(mesityl)₂(THF)₄ (Beno, Hope, Olmstead & Power, 1985).

We thank Dr A. J. M. Duisenberg for collecting the X-ray data. The investigations were supported in part (WJJS and ALS) by the Netherlands Foundation for

* 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 ⁱ	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 ⁱⁱ)	114.1 (2)	C(3)—C(4)—C(3)	122.0 (3)
N(1)—Li—C(1 ⁱⁱ)	131.17 (5)	N(1)—C(5)—C(2)	111.3 (2)
C(1)—Li—C(1 ⁱⁱ)	114.1 (2)	N(2)—C(8)—C(3)	113.4 (2)

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

Chemical Research (SON) with financial aid from the Netherlands Organization of Pure Research (ZWO).

References

- BENO, M. A., HOPE, H., OLMSTEAD, M. M. & POWER, P. P. (1985). *Organometallics*, **4**, 2117–2121.
- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
- JASTRZEBSKI, J. T. B. H., VAN KOTEN, G., GOUBITZ, K., ARLEN, C. & PFEFFER, M. (1983). *J. Organomet. Chem.* **246**, C75–C79.
- MCCANDLISH, L. E., STOUT, G. H. & ANDREWS, L. C. (1975). *Acta Cryst.* **A31**, 245–249.
- SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
- SHELDRICK, G. M. (1986). *SHELXS86*. Program for crystal structure determination. Univ. of Göttingen, Federal Republic of Germany.
- SPEK, A. L. (1982). The *EUCLID* package. In *Computational Crystallography*, edited by D. SAYRE, p. 528. Oxford: Clarendon Press.
- THOENNES, D. & WEISS, E. (1978). *Chem. Ber.* **111**, 3157–3161.
- ZEIJDEN, A. A. H. VAN DER, VAN KOTEN, G., SMEETS, W. J. J. & SPEK, A. L. (1987). *J. Organomet. Chem.* Submitted.

Acta Cryst. (1987). **C43**, 1430–1432

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

BY F. FLORENCIO AND S. GARCÍA-BLANCO

X-ray Department, Institute Rocasolano, CSIC, Madrid, Spain

(Received 3 June 1986; accepted 2 February 1987)

Abstract. C₁₅H₁₂N₂O, $M_r = 236.273$, orthorhombic, *Pbca*, $a = 22.866$ (2), $b = 13.173$ (1), $c = 8.517$ (1) Å, $V = 2565.3$ (2) Å³, $Z = 8$, $D_x = 1.2235$ g cm⁻³,

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

0108-2701/87/071430-03\$01.50

© 1987 International Union of Crystallography