Table 3. *Comparison of anhydrous octyl* α-D-*glucopyranoside with the hemihydrate and the monohydrate, and with anhydrous decyl* α-D-*glucopyranoside*

	Space group	*a* (Å)	*b* (Å)	*c* (Å)	*β* (°)	*Z*	*V*/*Z* (Å^3)
Octyl							
$C_{14}H_{28}O_6$*	*P*2$_1$	5·140 (2)	7·604 (2)	19·939 (4)	92·18 (2)	2	389·4
$C_{14}H_{28}O_6.0{\cdot}5\ H_2O$†	*C*2	15·190 (5)	5·136 (3)	19·944 (7)	92·74 (3)	4	388·6
$C_{14}H_{28}O_6.H_2O$‡	*C*2	17·829 (3) (8·011)	5·144 (2) (5·144)	18·262 (4) (20·322)	90·30 (2)	4	418·7
Decyl							
$C_{16}H_{32}O_6$§	*P*2$_1$	5·153 (2)	7·624 (4)	22·125 (7)	90·95 (4)	2	434·7

* This work.
† Jeffrey *et al.* (1987).
‡ Van Koningsveld *et al.* (1986). The subcell values are given within parentheses.
§ Moews & Knox (1976).

axis is parallel to the alkyl plane. Thus, all chains are parallel in the anhydrous crystal seen along **b**. The interwoven chains cross each other in both the hemihydrate and monohydrate crystals when viewed along **a**.

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Structure of *N,N*-Dimethyl-1,4-phenylenediamine

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Abstract. $C_8H_{12}N_2$, $M_r = 136{\cdot}2$, monoclinic, *P*2/*c*, $a = 10{\cdot}484\ (4)$, $b = 7{\cdot}342\ (2)$, $c = 21{\cdot}245\ (3)$ Å, $\beta = 90{\cdot}90\ (2)^\circ$, $V = 1635{\cdot}1\ (9)$ Å^3, $Z = 8$, $D_x = 1{\cdot}106$ Mg m^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}54178$ Å, $\mu(\mathrm{Cu}\ K\alpha) = 0{\cdot}53$ mm^{-1}, $F(000) = 592$, $T = 295$ K, $R = 0{\cdot}054$ for 2605 observed reflections $[F_o > \sigma(F_o)]$. Two independent molecules with almost the same geometries are included in the asymmetric unit. Amino and dimethylamino groups in the molecules adopt pyramidal structures. The angles between the bisector of the Me—N—Me angle and extension of the bond C(*ipso*)—N(dimethylamino) are 41·7 and 42·2° for the two molecules, respectively. Comparison with the molecular structure in the complex with 1,2,4,5-tetracyanobenzene revealed less contribution from a quinoidal form to the structures in free molecules. Hydrogen bonds were found between the H atoms of the amino groups and the N atoms in the amino and the dimethylamino groups.

Introduction. We have been interested in the substituent effect on the planarity of amino groups or dimethylamino groups in six-membered aromatics. The structure of one of them, the title compound, was determined by X-ray analysis.

The title compound is a strong electron donor and easily forms charge-transfer complexes with electron acceptors. We were interested in the effect of complex formation on the molecular structure of the donor. Therefore, the structure of the free molecule was compared with that in the complex with 1,2,4,5-tetracyanobenzene (Ohashi, 1973).

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Experimental. Colorless prism crystals obtained by slow sublimation *in vacuo*. Single crystal (0·3 × 0·4 × 0·6 mm) tightly held in a glass capillary (about 0·4 mm ∅ with 1/100 mm thickness). Rigaku AFC-5R diffractometer, graphite-monochromatized Cu $K\alpha$. Cell dimensions from 2θ angles for 25 reflections ($29 < 2\theta < 38°$). Intensities measured up to $2\theta = 140°$ in h 0/12, k −8/0 and l −25/25. Three standard reflections monitored every 100 measurements (±1% variation). 3005 unique reflections measured, 2605 intensities observed [$F_o \leq \sigma(F_o)$ and seven very strong reflections were rejected], no absorption corrections. Structure solved by *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). H atoms located on a difference density map. Positional parameters of all atoms and anisotropic thermal parameters of non-H atoms refined by block-diagonal least squares. Temperature factor of each H atom equal to $B_{\rm eq}$ of the bonded atom. $\sum(w^2|\Delta F|^2)$ minimized, $w^2 = 1/[\sigma^2(F_o) + 0{\cdot}00319|F_o|^2]$, $w = 0$ for 41 reflections with $w|\Delta F| \geq 3$. Final $R = 0{\cdot}054$, $wR = 0{\cdot}069$, $S = 0{\cdot}9857$. No significant peaks in final difference map, highest peak 0·25 e Å^{-3}. Max. Δ/σ in the final cycle 0·11. Atomic scattering factors calculated by $\sum[a_i\exp(-b_i\lambda^{-2}\sin^2\theta)] + c$ $(i = 1,\ldots,4)$ (*International Tables for X-ray Crystallography,* 1974). Calculations performed by FACOM M340R computer at Shionogi Research Laboratories.

Discussion. Two independent molecules were observed in the crystal. Their atomic coordinates and equivalent isotropic temperature factors are listed in Table 1. Bond lengths and angles are given in Table 2.* A perspective view of molecules *A* and *B* with the atom-labeling system and a stereoview of the crystal packing drawn using the program *PLUTO* (Motherwell & Clegg, 1978) are presented in Figs. 1 and 2, respectively. The geometries of both molecules are very similar.

The two H(amino) atoms in both molecules form hydrogen bonds with N atoms in an amino and a dimethylamino group of adjacent molecules: (N10)H···N(10′) (x, $y-1$, z) = 2·24 (2) [N···N 3·146 (3)], (N10)H′···N(7) (x, $y-1$, z) = 2·34 (2) [3·270 (3)], (N10′)H···N(10) ($1-x$, $1+y$, $\frac{1}{2}-z$) = 2·29 (2) [3·173 (3)] and (N10′)H′···N(7′) (x, $1+y$, z) = 2·25 (2) Å [3·228 (3) Å]. The crystal structure is composed of networks of the hydrogen bonds.

Table 1. *Atomic coordinates and equivalent isotropic temperature factors* (Å^2) *with e.s.d.'s in parentheses*

$$B_{\rm eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
Molecule *A*				
C(1)	0·6181 (1)	−0·0099 (2)	0·1285 (1)	4·51 (3)
C(2)	0·6521 (1)	0·1326 (2)	0·1680 (1)	4·69 (3)
C(3)	0·6818 (1)	0·3023 (2)	0·1445 (1)	4·83 (3)
C(4)	0·6791 (1)	0·3381 (2)	0·0801 (1)	4·58 (3)
C(5)	0·6432 (2)	0·1958 (2)	0·0408 (1)	5·49 (4)
C(6)	0·6136 (2)	0·0260 (2)	0·0645 (1)	5·55 (4)
N(7)	0·7070 (1)	0·5159 (2)	0·0572 (1)	5·75 (4)
C(8)	0·6908 (2)	0·5408 (3)	−0·0111 (1)	7·76 (6)
C(9)	0·8284 (2)	0·5896 (3)	0·0802 (1)	8·64 (7)
N(10)	0·5840 (1)	−0·1825 (2)	0·1519 (1)	5·89 (4)
Molecule *B*				
C(1)	0·7355 (1)	0·5757 (2)	0·3063 (1)	4·60 (3)
C(2)	0·6543 (1)	0·4342 (2)	0·3215 (1)	4·84 (3)
C(3)	0·7011 (1)	0·2643 (2)	0·3367 (1)	5·06 (4)
C(4)	0·8316 (1)	0·2273 (2)	0·3373 (1)	4·74 (3)
C(5)	0·9122 (1)	0·3679 (2)	0·3208 (1)	5·57 (4)
C(6)	0·8648 (1)	0·5381 (2)	0·3054 (1)	5·65 (4)
N(7)	0·8765 (1)	0·0484 (2)	0·3523 (1)	5·98 (4)
C(8)	1·0145 (2)	0·0216 (3)	0·3462 (1)	8·39 (7)
C(9)	0·8298 (3)	−0·0217 (3)	0·4119 (1)	9·05 (8)
N(10)	0·6884 (1)	0·7489 (2)	0·2895 (1)	5·94 (4)

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

	Molecule *A*	Molecule *B*
C(1)—C(2)	1·384 (3)	1·385 (3)
C(1)—C(6)	1·385 (3)	1·384 (3)
C(1)—N(10)	1·409 (3)	1·408 (3)
C(2)—C(3)	1·380 (3)	1·377 (3)
C(3)—C(4)	1·393 (3)	1·395 (3)
C(4)—C(5)	1·386 (3)	1·383 (3)
C(4)—N(7)	1·425 (3)	1·430 (3)
C(5)—C(6)	1·382 (3)	1·382 (3)
N(7)—C(8)	1·470 (3)	1·468 (3)
N(7)—C(9)	1·460 (3)	1·459 (4)
C(2)—C(1)—C(6)	117·1 (2)	117·4 (2)
C(2)—C(1)—N(10)	122·0 (2)	121·5 (2)
C(6)—C(1)—N(10)	120·8 (2)	121·1 (2)
C(1)—C(2)—C(3)	121·4 (2)	121·1 (2)
C(2)—C(3)—C(4)	121·6 (2)	121·6 (2)
C(3)—C(4)—C(5)	116·8 (2)	117·1 (2)
C(3)—C(4)—N(7)	120·5 (2)	120·0 (2)
C(5)—C(4)—N(7)	122·7 (2)	122·8 (2)
C(4)—C(5)—C(6)	121·4 (2)	121·1 (2)
C(1)—C(6)—C(5)	121·7 (2)	121·7 (2)
C(4)—N(7)—C(8)	115·5 (2)	115·2 (2)
C(4)—N(7)—C(9)	114·1 (2)	113·8 (2)
C(8)—N(7)—C(9)	111·8 (2)	112·0 (2)

The phenyl rings in both molecules are planar and N atoms lie on these planes. Torsion angles C(3)—C(4)—N(7)—C(9) and C(5)—C(4)—N(7)—C(8) are respectively 53·4 (3) and 2·1 (3)° for molecule *A*, 53·8 (3) and 2·7 (3)° for molecule *B*. These values show about 28° rotation of the respective dimethylamino group around the bond C(4)—N(7) from the conformation in which those two torsion angles have the same absolute value with opposite sign to each other. On the other hand, the amino groups do not rotate.

The amino and the dimethylamino groups are pyramidal forms, and the lone-pair orbitals on the N atoms in these groups are oriented on the same side of the phenyl-ring plane in the respective molecules. The planarity of the amino and the dimethylamino groups is conveniently defined by φ, where φ is the angle between the bisector of the angle Me—N—Me or H—N—H and

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* Lists of structure factors, atomic coordinates of the H atoms and anisotropic temperature factors of the non-H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44762 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

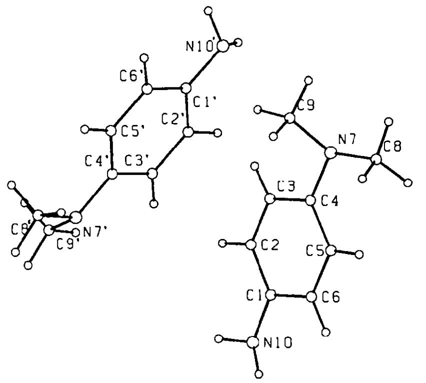

Fig. 1. Perspective view with the atom-labeling system for *N*,*N*-dimethyl-1,4-phenylenediamine. The atom labels are primed for molecule *B*.

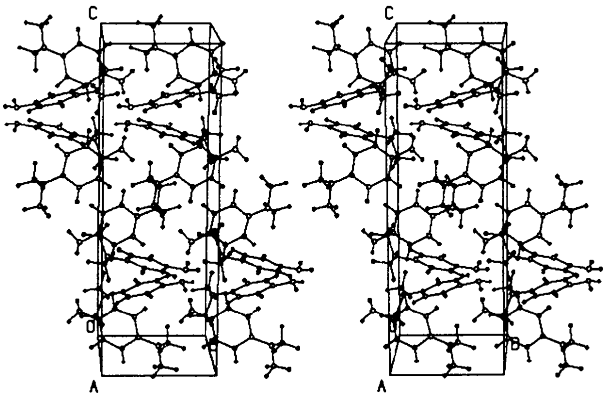

Fig. 2. A stereoview of the unit-cell packing.

the extension of the bond C(*ipso*)—N (Christen, Norbury, Lister & Palmieri, 1975). The values of φ(dimethylamino) and φ(amino) are respectively 41·7 and 48·2° for molecule *A*, and 42·2 and 45·0° for molecule *B*. The corresponding values in the complex with 1,2,4,5-tetracyanobenzene are 29·0 and 25·3°. Thus, the planarities of the amino and the dimethylamino groups increase on complex formation. One of the most probable reasons for this is the disappearance of hydrogen bonds to the lone-pair electrons on the N atoms. In comparison with the complex, bond lengthening was observed in the molecular structures; C(2)—C(3), C(5)—C(6) and C(4)—N(7) are longer than 1·358 (7), 1·376 (7) and 1·412 (6) Å in the complex, respectively. Thus, the contribution of a quinoidal form to the molecular structure is less than that in the complex. This finding supports the decrease in conjugation between the phenyl ring and the dimethylamino group resulting from the increase in the non-planarity of the group. In addition, this increase would lead to a decrease of hyperconjugation between the methyl groups and the lone-pair orbital on the N atom. In fact, the N—Me bond distances are longer than 1·445 (7) and 1·441 (8) Å in the complex.

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Structure of the Quasi-equatorial Isomer of 5,11-Dinitrohexacyclo[5.4.1.$0^{2,6}$.$0^{3,10}$.$0^{4,8}$.$0^{9,12}$]dodecane and Crystal Density Calculations for Several Di-, Tri- and Tetranitro Analogs

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Abstract. $C_{12}H_{12}N_2O_4$, $M_r = 248·24$, monoclinic, $C2/c$, $a = 25·448$ (2), $b = 9·165$ (1), $c = 17·248$ (5) Å, $\beta = 127·35$ (2)°, $V = 3198$ (1) Å^3, $D_x = 1·547$ g cm^{-3} for $Z = 12$, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 1·3$ cm^{-1}, $F(000) = 1560$ e, $T = 294$ K, diffractometer data, 2927 unique data, 1440 $I > 3\sigma(I)$, $R = 0·045$. Eight molecules are in general positions; four are in special positions on the crystallographic dyads. Each molecule contains one

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