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Structure of N,N'-Diphenyl-2,4-hexadiyne-1,6-diamine

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Abstract. $C_{18}H_{16}N_2$, $M_r = 260.3$, monoclinic, $P2_1/c$, $a = 8.740$ (4), $b = 16.858$ (9), $c = 9.915$ (5) Å, $\beta = 99.02$ (4)°, $V = 1443$ (1) Å^3, $Z = 4$, $D_x = 1.198$ g cm^{-3}, $\lambda(Mo\ K\alpha) = 0.71069$ Å, $\mu(Mo\ K\alpha) = 0.8$ cm^{-1}, $F(000) = 552$, $T = 150$ K, $R = 0.067$ using 2603 independent observed reflections. The molecules have pseudo-*cis* configuration and are linked in the crystal *via* N—H⋯N hydrogen bonds to form infinite double chains. The absence of a stacking arrangement of the 1,3-butadiyne groups of neighbouring molecules is consistent with the observed inertness of the compound to solid-state polymerization.

Introduction. Some derivatives of diacetylene (1,3-butadiyne) exhibit a structurally determined ability to undergo solid-state polymerization (Wegner, 1977). As part of a study on the relation between crystal structure and solid-state reactivity of diacetylenes we carried out a single-crystal X-ray study of N,N'-diphenyl-2,4-hexadiyne-1,6-diamine, which is stable to UV and γ-radiation.

Experimental. Pale yellow prismatic crystal, dimensions $0.3 \times 0.3 \times 0.8$ mm, used for measurement of unit-cell parameters (24 reflections with $25 \le 2\theta \le 28°$) and intensities of 3273 reflections ($-11 \le h \le 11$, $0 \le k \le 21$, $0 \le l \le 12$) with Syntex $P2_1$ diffractometer (Mo $K\alpha$, graphite monochromator, $\theta/2\theta$ scan, $2\theta_{max} = 55°$). No significant variation in intensities of 3

standard reflections (100, 020, 004) measured after every 100 reflections. No absorption and secondary-extinction corrections. Structure solved by direct methods, revealing all non-hydrogen atoms, and refined by full-matrix least squares with anisotropic thermal parameters for non-hydrogen atoms, using 2603 independent reflections with $I \ge 2\sigma(I)$ and minimizing $\sum w(|F_o| - |F_c|)^2$, $w = 1/[\sigma^2(F_o) + (F_c)^2]$. Scattering factors from *International Tables for X-ray Crystallography* (1974). Hydrogen atoms located by difference Fourier synthesis and refined isotropically. $R = 0.067$, $wR = 0.072$, $S = 5.23$, max. (shift/σ) = 0.5, final electron-density fluctuations ± 0.4 e Å^{-3}. All calculations carried out with an Eclipse S/200 computer using *INEXTL* programs (Gerr, Yanovsky & Struchkov, 1983).†

Discussion. The positional and thermal atomic parameters are listed in Table 1; the atom numbering, bond lengths and main bond angles are shown in Fig. 1. A full list of bond angles involving non-hydrogen atoms is given in Table 2.

The molecule has a non-symmetrical pseudo-*cis* configuration unusual for symmetrically substituted diacetylenes; the pseudo torsion angles N(1)C(1)-

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† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42691 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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C(6)N(2) and C(10)C(1)C(6)C(16) are −59·8 (6) and 23·2 (2)° respectively.

The lengths of the triple C≡C bonds [1·191 and 1·189 (7) Å], the single ≡C—C≡ and —C—C≡ bonds [1·378 and 1·479, 1·482 (7) Å], and the bond angles C≡C—C [178·2 and 179·5 (5)°] and C—C≡C [175·6 and 177·5 (5)°] are unexceptional for diacetylenes. In the centrosymmetric molecule of 2,4-hexadiyne-1,6-diyl bis[p-(pentyloxy)benzoate], the corresponding values are 1·187, 1·367, 1·473 (7) Å and 179·1, 174·8 (5)° (Shklover, Struchkov, Bagirov, Konstantinov & Amerik, 1985).

The N(1)—C(1) and N(2)—C(6) bond lengths of 1·467 (6) and 1·453 (6) Å respectively are close to the N—CH$_2$ distances of 1·458 and 1·464 (4) Å in the molecule poly[1,2-bis(diphenylaminomethyl)-1-buten-3-ynylene] (Enkelmann & Schleier, 1980). The N(1)—C(7) and N(2)—C(13) bond lengths of 1·411 (6) and 1·381 (6) Å respectively are close to the (CH$_2$)N—C(Ph) distances of 1·411–1·418 (4) Å in poly[1,2-bis(diphenylaminomethyl)-1-buten-3-ynylene] and to the H$_2$N—C(Ph) distances of 1·398 and 1·386 (6) Å in aniline (two crystallographically independent molecules; Fukuyo, Hirotsu & Higuchi, 1982).

The dihedral angle between the plane of the phenyl ring C(7)···C(12) and the C(1)N(1)C(7) plane is 15·9 (4)°, and the angle between the plane of the C(13)···C(18) ring and the C(6)N(2)C(13) plane is 8·3 (4)°.

The slightly shortened N(2)—C bonds [in comparison with the N(1)—C bonds] and coplanarity of the C(13)···C(18) phenyl ring with the N(2) coordination plane indicate a π interaction between the N(2) lone pair and the phenyl ring.

The molecules are linked via N(2)—H(N2)···N(1) (−x, ½ + y, ½ − z) hydrogen bonds to form infinite double chains along the b axis in a head-to-tail pattern. These hydrogen bonds [N(2)···N(1) 3·057 (7), H(N2)···N(1) 2·31 (7) Å, N(2)H(N2)N(1) 171 (2)°] are stronger than in the aniline crystal [N···N 3·180 (6) and 3·373 (5) Å, H···N 2·165 (5) and 2·43 (3) Å, NHN 159 (4) and 158 (3)°]. The angles C(1)N(1)··· H(N2), C(7)N(1)···H(N2) and H(N1)N(1)···H(N2) are 114 (1), 94 (1) and 104 (3)° respectively, i.e. this hydrogen bond is directed approximately towards the lone electron pair of the acceptor N(1) atom, whose hydrogen atom does not participate in hydrogen bonds. Fig. 2 shows the crystal structure in the ab projection.

The approximately planar moieties [the phenyl ring C(13)···C(18) and amino group C(6)N(2)C(13)] of the molecules in neighbouring chains, related by the inversion centre at (½,0,½), are close to each other. In particular, some of the intermolecular distances, viz C(6)···C(13)(−1 − x, −y, 1 − z), 3·357 (7) Å, and C(6)···C(14)(−1 − x, −y, 1 − z), 3·368 (7) Å, are shorter than double the van der Waals radius of the C atom (3·60 Å) (Kitaigorodsky, 1973).

Table 1. *Atomic coordinates* (×10⁴, *for* H ×10³) *and equivalent isotropic or isotropic* (*for* H *atoms*) *thermal parameters* (Å²)

$$B_{eq} = \tfrac{1}{3}\sum_i\sum_j b_{ij} a_i^* a_j^* (\mathbf{a}_i.\mathbf{a}_j).$$

	x	y	z	B_{eq} or B_{iso}
N(1)	978 (4)	3586 (2)	1611 (4)	2·03 (9)
N(2)	−3028 (5)	−188 (2)	4552 (4)	2·3 (1)
C(1)	284 (6)	2988 (3)	627 (5)	2·5 (1)
C(2)	−576 (5)	2356 (3)	1222 (5)	2·3 (1)
C(3)	−1291 (6)	1883 (3)	1762 (4)	2·1 (1)
C(4)	−2154 (5)	1336 (3)	2352 (4)	2·1 (1)
C(5)	−2907 (5)	869 (3)	2860 (4)	2·2 (1)
C(6)	−3869 (6)	272 (3)	3436 (5)	2·4 (1)
C(7)	2111 (5)	3342 (3)	2706 (4)	2·0 (1)
C(8)	2523 (6)	3874 (3)	3784 (5)	2·4 (1)
C(9)	3730 (6)	3699 (3)	4816 (5)	2·9 (1)
C(10)	4521 (6)	2984 (3)	4805 (5)	2·9 (1)
C(11)	4109 (5)	2455 (3)	3756 (5)	2·9 (1)
C(12)	2903 (5)	2623 (3)	2717 (5)	2·3 (1)
C(13)	−2586 (5)	127 (3)	5840 (4)	1·9 (1)
C(14)	−3061 (5)	877 (3)	6223 (5)	2·1 (1)
C(15)	−2713 (6)	1112 (3)	7579 (5)	2·9 (1)
C(16)	−1861 (6)	642 (3)	8552 (5)	2·9 (1)
C(17)	−1342 (6)	−92 (3)	8160 (5)	2·8 (1)
C(18)	−1661 (6)	−339 (3)	6834 (5)	2·3 (1)
H(N1)	18 (8)	390 (4)	182 (7)	7 (2)
H(N2)	−260 (7)	−53 (4)	425 (6)	6 (2)
H(1·1)	108 (4)	278 (2)	18 (4)	1·0 (7)
H(1·2)	−32 (7)	320 (3)	−12 (6)	5 (1)
H(6·1)	−482 (6)	54 (3)	373 (5)	3 (1)
H(6·2)	−412 (6)	−8 (3)	278 (5)	4 (1)
H(8)	195 (6)	438 (3)	378 (6)	4 (1)
H(9)	390 (5)	406 (3)	557 (5)	2 (1)
H(10)	520 (6)	293 (3)	548 (5)	3 (1)
H(11)	461 (5)	194 (3)	375 (5)	3 (1)
H(12)	276 (5)	230 (3)	204 (4)	2 (1)
H(14)	−354 (6)	124 (3)	556 (5)	3 (1)
H(15)	−296 (4)	158 (2)	780 (4)	1·0 (8)
H(16)	−170 (6)	82 (2)	947 (5)	3 (1)
H(17)	−73 (6)	−42 (3)	883 (6)	4 (1)
H(18)	−153 (5)	−86 (3)	654 (5)	2 (1)

Table 2. *Bond angles involving non-*H *atoms* (°)

C(1)C(2)C(3)	175·6 (5)	C(4)C(5)C(6)	177·6 (5)
C(2)C(3)C(4)	178·2 (5)	C(3)C(4)C(5)	179·5 (5)
N(1)C(1)C(2)	114·4 (4)	N(2)C(6)C(5)	113·9 (4)
C(1)N(1)C(7)	118·6 (4)	C(6)N(2)C(13)	122·2 (4)
N(1)C(7)C(8)	117·8 (4)	N(2)C(13)C(18)	118·6 (4)
N(1)C(7)C(12)	123·1 (4)	N(2)C(13)C(14)	123·1 (4)
C(7)C(8)C(9)	120·3 (4)	C(13)C(14)C(15)	119·3 (4)
C(8)C(9)C(10)	120·1 (5)	C(14)C(15)C(16)	121·9 (5)
C(9)C(10)C(11)	119·8 (5)	C(15)C(16)C(17)	118·6 (5)
C(10)C(11)C(12)	120·6 (5)	C(16)C(17)C(18)	120·9 (5)
C(11)C(12)C(7)	120·2 (4)	C(17)C(18)C(13)	120·7 (4)
C(12)C(7)C(8)	118·9 (4)	C(18)C(13)C(14)	118·3 (4)
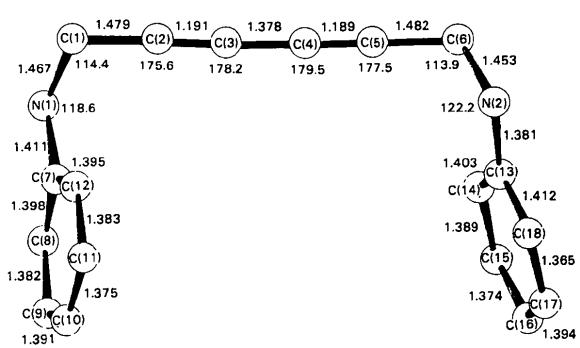
Fig. 1. Structure of the molecule with bond lengths (e.s.d.'s 0·006–0·007 Å) and relevant bond angles (e.s.d.'s 0·4–0·5°).
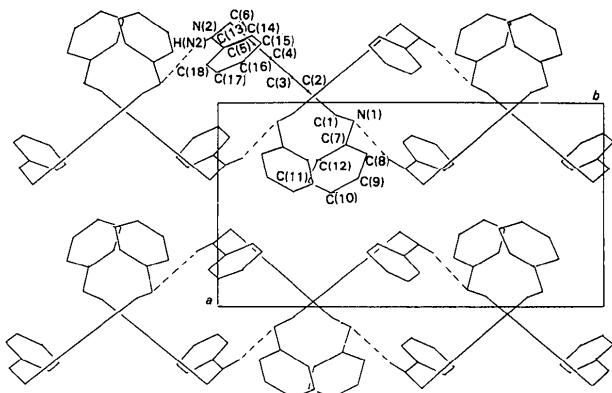
Fig. 2. Crystal structure in the *ab* projection.

The stacking arrangement and direct intermolecular contacts of the diacetylene rods, which are characteristic for reactive (in particular polymerizable) diacetylenes in the solid state, are absent [the shortest distances between diacetylene groups are C(2)···C(3)-(x, $y + \frac{1}{2}$, $z - \frac{1}{2}$), 4·553 (7) Å, and C(2)···C(4)(x, $y + \frac{1}{2}$, $z - \frac{1}{2}$), 4·453 (7) Å].

The packing of the molecules in the crystal is apparently governed primarily by the hydrogen bonds mentioned above and by short intermolecular contacts between the molecular chains, which prevent further mutual approach of the diacetylene rods. The observed peculiarities of the molecular packing are consistent with the observed inertness of the title compound to solid-state polymerization.

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Structure of Dodecyldimethylpropylammonium Bromide Monohydrate

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Abstract. $[C_{17}H_{38}N]Br.H_2O$, $M_r = 354·4$, triclinic, $P\bar{1}$, $a = 8·234$ (1), $b = 8·502$ (1), $c = 17·494$ (1) Å, $\alpha = 84·96$ (1), $\beta = 78·41$ (1), $\gamma = 61·24$ (1)°, $V = 1051·7$ (2) Å³, $Z = 2$, $D_x = 1·12$ Mg m⁻³, $\lambda(Cu\, K\alpha) = 1·54178$ Å, $\mu = 2·64$ mm⁻¹, $F(000) = 384$, $T = 295$ K, $R = 0·046$ for 3119 reflections. The long hydrocarbon chains are fully extended in a zigzag form, and have an antiparallel arrangement in a triclinic subcell. The Br ions exist near the N atoms of the hydrocarbon chains. The two Br ions and two water molecules form a large divalent anionic group, held together by Br···O hydrogen bonds.

Introduction. As part of an investigation on the crystal properties and molecular packing of alkylammonium halides with various lengths of alkyl chains, the crystal structure of the title compound was determined. Dodecyldimethylpropylammonium bromide crystallizes in several different hydrate forms. In the present study of the monohydrate form, the role of the water molecules in the crystal structure was of particular interest.

Experimental. Crystal grown from ethyl acetate solution, needle-shaped transparent prism, 0·15 × 0·2 × 0·3 mm. Rigaku AFC-5RU diffractometer, graphite-monochromated Cu $K\alpha$ radiation; lattice parameters from 20 reflections with $18 < \theta < 26°$; three standard reflections measured every 56 reflections, no significant change in intensities; 3210 unique