Acta Cryst. (1977). B**33**, 3531–3533

1,4-Diethynylnaphthalene

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(*Received* 21 *March* 1977; *accepted* 28 *April* 1977)

Abstract. $(C_{14}H_8)_2$, orthorhombic, $Pca2_1$, a = 31·065 (10), b = 4·024 (2), c = 15·638 (6) Å, Z = 4, D_x = 1·20, D_m = 1·20 g cm^{-3}. The asymmetric unit contains two independent molecules.

Introduction. The collection of intensity data was carried out on a Siemens automatic four-circle diffractometer using Cu $K\alpha$ radiation. The θ–2θ scan mode was used (five-point method). Of the 1942 accessible, not systematically extinct, unique reflexions, significant counts were recorded for 1261 ($2\theta < 140°$). Systematic absences were $0kl$ for l odd and $h0l$ for h odd. Of the four possible space groups $Pbcm$, $Pbam$, $Pba2$ and $Pca2_1$, the last was chosen on the basis of the centricity test of Ramachandran & Srinivasan (1959) and from packing considerations (Kitaigorodskii, 1961). This assumption was verified by the final structural results. The structure was solved by direct methods with the program *MULTAN* (Declercq, Germain, Main & Woolfson, 1973). Refinement was by full-matrix least-squares analysis. The quantity minimized was $\Sigma w(F_o - F_c)^2$. On termination of refinement the weighted R index was 0·042; the conventional R index at this stage was 0·062. The weights applied in the least-squares analysis were $1/[\sigma(F)]^2$, where $\sigma(F)$ was derived from the counting statistics. The H atoms were assigned reasonable parameters and their contributions were included in structure factor calculations. No absorption correction was applied. The programs used were those of the XRAY 76 system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). Scattering factors for C were from *International Tables for X-ray Crystallography* (1968) and for H from Stewart, Davidson & Simpson (1965). The final atomic and (for H only) thermal parameters are given in Table 1.*

Discussion. 1,4-Diethynylnaphthalene is of interest because it is known to polymerize in the solid state (Ried & Wesselborg, 1961). This study was undertaken to assist investigation of the mechanism of this reaction. It was of particular interest to know whether the molecular packing allows reaction of neighbouring molecules in a manner similar to the topochemical

Table 1. *Final atomic parameters* (× 10^4)

H atom coordinates were not refined. For each H atom B_{iso} = 5·0 Å^2.

	x	y	z
C(1)	7814 (2)	3585 (20)	3940*
C(2)	7642 (2)	1982 (21)	3232 (6)
C(3)	7903 (3)	1072 (22)	2541 (6)
C(4)	8329 (3)	1812 (21)	2531 (5)
C(5)	8527 (2)	3494 (20)	3247 (5)
C(6)	8970 (3)	4326 (20)	3263 (6)
C(7)	9140 (3)	5928 (25)	3956 (7)
C(8)	8881 (3)	6715 (25)	4667 (6)
C(9)	8453 (3)	6009 (22)	4673 (5)
C(10)	8263 (2)	4347 (19)	3967 (6)
C(11)	7533 (3)	4447 (22)	4654 (6)
C(12)	7290 (3)	5182 (28)	5188 (6)
C(13)	8589 (3)	839 (25)	1798 (6)
C(14)	8806 (4)	−79 (31)	1225 (7)
C(15)	5785 (2)	6253 (20)	3932 (5)
C(16)	6219 (3)	5770 (20)	3999 (5)
C(17)	6507 (2)	6888 (21)	3388 (5)
C(18)	6358 (2)	8569 (19)	2661 (5)
C(19)	5909 (2)	9145 (19)	2566 (5)
C(20)	5741 (3)	10853 (21)	1840 (5)
C(21)	5319 (3)	11375 (24)	1756 (6)
C(22)	5021 (3)	10304 (25)	2365 (7)
C(23)	5166 (3)	8589 (21)	3083 (6)
C(24)	5613 (2)	7989 (18)	3190 (6)
C(25)	5494 (3)	4971 (22)	4576 (6)
C(26)	5264 (3)	3732 (25)	5085 (7)
C(27)	6661 (3)	9734 (22)	2032 (5)
C(28)	6898 (3)	10781 (27)	1512 (6)
H(1)	7301	1427	3231
H(2)	7764	9812	1993
H(3)	9172	3688	2721
H(4)	9477	6516	3968
H(5)	9016	7965	5212
H(6)	8254	6630	5209
H(7)	7067	5895	5688
H(8)	9006	9000	718
H(9)	6342	4484	4547
H(10)	6849	6478	3474
H(11)	5966	1729	1361
H(12)	5200	2700	1202
H(13)	4681	721	2294
H(14)	4942	7708	3564
H(15)	5054	2584	5535
H(16)	7123	1729	1053

* Fixed to define the cell origin.

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* Lists of structure factors and anisotropic temperature factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32876 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

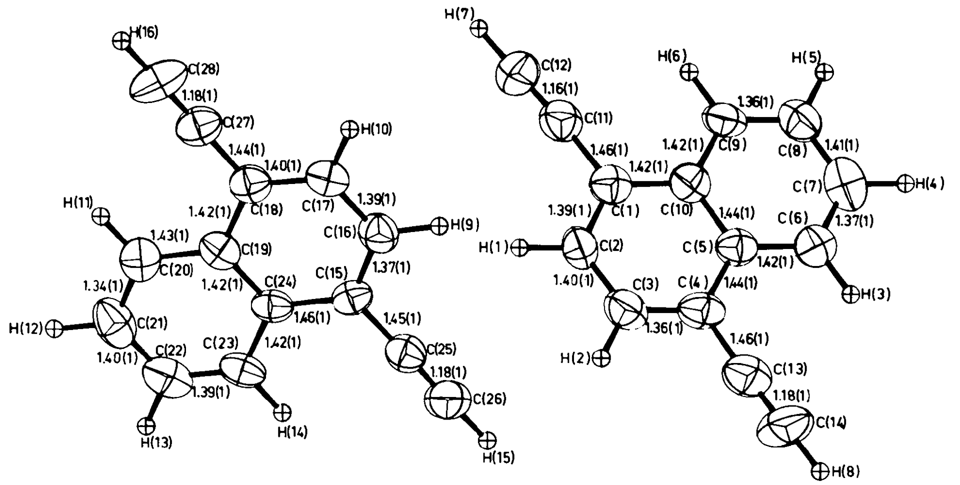

Fig. 1. The asymmetric unit with observed bond lengths (e.s.d.'s in parentheses) viewed along **b** (Johnson, 1965). The thermal vibration ellipsoids represent 50% probability.

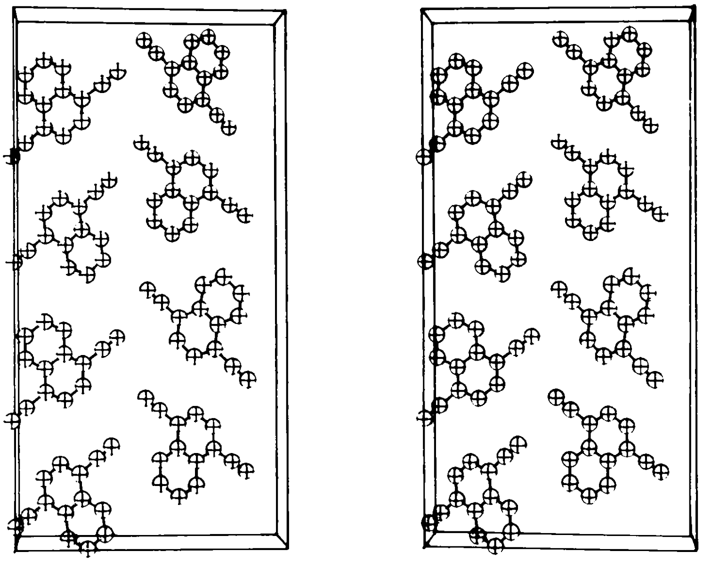

Fig. 2. Stereoscopic diagram of the unit cell. **c** is horizontal and **a** is vertical.

polymerization of diacetylenes (Wegner, 1972). Fig. 1 shows the asymmetric unit with the observed bond lengths. Bond angles in the naphthalene rings range from 118·0 to 122·6°. The acetylene bonds are not strictly linear [angles from 175·8 (10) to 177·5 (10)°]. It is interesting to note that two independent molecules make up the asymmetric unit. The same result has been reported for 1,4-dibromonaphthalene (Trotter, 1961).

Within the experimental error, bond lengths and angles of the two molecules are identical and do not differ significantly from those found in naphthalene (Cruickshank, 1957). The angle between the molecules is 58·3°. Fig. 2 shows a stereoscopic packing diagram. From the observed molecular arrangement it can be concluded that polymerization in 1,4-diethynylnaphthalene cannot proceed as a topochemical reaction but rather is connected with diffusion processes.

We thank Dr E. Hädicke, Badische Anilin- und Soda-Fabrik AG, Ludwigshafen, for his help in obtaining the intensity data. We also acknowledge the kind interest taken by Professor Dr G. Wegner in this study. Calculations were performed at the Rechenzentrum der Universität Freiburg and were supported by the Deutsche Forschungsgemeinschaft (DFG project We 698/3).

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Acta Cryst. (1977). B**33**, 3533–3535

Orthorhombic Barium Dihydrogenphosphate

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(*Received* 8 *March* 1977; *accepted* 5 *June* 1977)

Abstract. $Ba(H_2PO_4)_2$, space group *Pccn*, a = 7·7962 (10), b = 10·2574 (10), c = 8·5653 (11) Å at 295 K (λ = 1·54051 Å), Z = 4, D_x = 3·212, D_m = 3·21 g cm^{-3}. A corrugated network of hydrogen-bonded phosphate groups lies parallel to the *ac* plane with Ba–O coordination bonds running between the phosphate layers. The eight Ba–O distances range from 2·659 (2) to 2·903 (2) Å. The phosphate distances are: P–OH 1·579 (2) and 1·576 (2) Å, and P–O 1·495 (2) and 1·490 (2) Å.

Introduction. Colorless rhombic platelets of $Ba(H_2PO_4)_2$ were grown by slow evaporation from a solution of 10 g of barium phosphate in 200 g of a 10% aqueous solution of H_3PO_4. The space group, *Pccn*, is indicated by *mmm* Laue symmetry with systematic absences for 0*kl* and *h*0*l* (*l* odd) and *hk*0 (*h* + *k* odd). Crystal density was measured by flotation in a mixture of tetrabromoethane and diiodomethane.

The data crystal was cut to 0·5 × 0·45 × 0·45 mm and mounted on a four-circle automated diffractometer with φ approximately along [320]. Cell constants were determined by least-squares fit from 2θ, ω and χ values measured with the resolved Cu $K\alpha_1$ line for 25 reflections in the range $73° < 2\theta < 88°$. Intensity data for 5792 reflections were measured out to $2\theta = 90°$ by θ–2θ step scans (step interval 2θ = 0·05°) using a 0·001 in Nb filter with Mo $K\alpha$ radiation (*hkl* and $\bar{h}\bar{k}\bar{l}$ octants were measured). Reflections with $2\theta < 16°$ were measured with Y–Zr balanced filters (here $\pm h \pm k \pm l$ were measured). Counts were made for 2 s at each step with 10 s background counts at the end of each scan. As provided in the diffractometer control program (Lenhert, 1975), a dead-time correction was applied to each step and each scan was repeated once with background counting time increased to 20 s if $I/\sigma(I)$ was less than 10. Total X-ray exposure (50 kV, 10 mA, tube focal spot 15 × 0·75 mm) was 350 h, during which time three standard reflections showed an intensity decrease of 1%.

Symmetry-related reflections were averaged to give 2846 F_o values (82 with $F_o < 0$, which were set to zero). Absorption corrections were calculated by the computer program *ORABS* (Wehe, Busing & Levy, 1962) using a linear absorption coefficient of 6·258 cm^{-1} and an 8 × 8 × 8 Gaussian grid. The maximum, minimum and average transmission factors were 0·210, 0·091 and 0·164. Further details of the data-collection and data-reduction procedures have been published previously (Miller, Lenhert & Joesten, 1972).