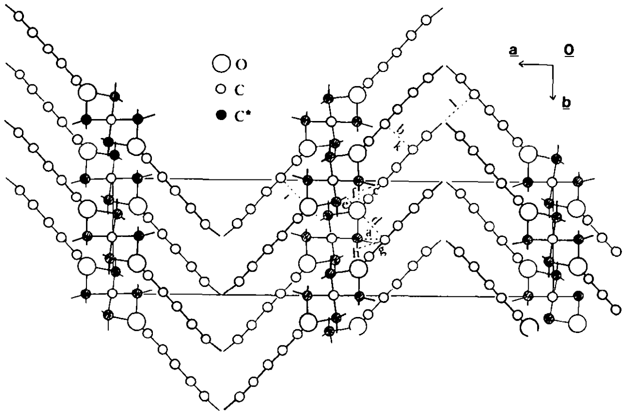

Fig. 2. Packing in the structure viewed along **c**. Partially occupied positions of C(6) and C(7) which coincide in this projection are hatched (C*).

the molecule in the structure together with the pseudo-C_2 conformation of the seven-membered rings joined by the spiro atom results in the pseudo-D_2 symmetry of the whole molecule.

The molecular structure observed is more consistent with the name 'spiran' (meaning pretzel in Latin) than the orthogonal conformations found in other structures such as *N*,*N*-dimethylspiro[5*H*-dibenzo[*a*,*d*]cycloheptene-5,1'-cyclohexane]-4'-amine (Rodgers, Kennard & Sheldrick, 1976) and (±)-2,2'-spirobi(indan)-1,1'-dione (Petersen & Danielsen, 1974).

The packing in the structure given in Fig. 2 shows that the disordered atoms are not in close contact. They interact primarily with the planar part of the neighbouring molecules so that the environment of the partially occupied positions is the same. The shortest intermolecular approach is H(72) to H(2) in $(x, \frac{1}{2}+y, -\frac{1}{2}+z)$ at 2·11 Å. All other H···H distances are greater than 2·59 Å.

We are greatly indebted to Professor Smolinski for suggesting the problem and providing the crystals.

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Bis(*p*-nitrophenyl)butadiyne

By J. J. Mayerle, T. C. Clarke and K. Bredfeldt

IBM Research Laboratory, San Jose, California 95193, *USA*

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Abstract. $C_{16}H_8N_2O_4$, M_r = 292·24, tetragonal, $I4_1/amd$, a = 7·088 (1), c = 26·785 (5) Å, Z = 4, D_c = 1·44, D_o = 1·44 (1) Mg m^{-3}. The phenyl rings on opposite ends of the molecules are mutually perpendicular. The packing arrangement is one of interpenetrating stacks of molecules arrayed along a and b in a manner that renders the molecules inert to solid-state polymerization.

Introduction. The solid-state polymerization of diacetylenes has been of considerable interest recently. This reaction, extensively studied by Wegner (1977) and co-workers, is illustrated in Fig. 1. Since this polymerization is often a single-crystal to single-crystal transformation, it readily lends itself to crystallographic analysis. We have taken advantage of this and studied several unreactive diacetylene monomers

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(Mayerle & Clarke, 1978; Mayerle & Flandera, 1978) to examine the influence of molecular packing on solid-state reactivity, the subtlety of which is richly illustrated by the contrast in reactivity between the readily polymerizable 2,4-hexadiynylene bis(*p*-toluenesulfonate) (Wegner, 1971*a*) and the closely related, but inert, 2,4-hexadiynylene bis(*p*-chlorobenzenesulfonate) (Mayerle & Clarke, 1978).

In a study of the reactivity of diphenyldiacetylene derivatives containing polar or hydrogen-bonding substituents, Wegner (1971*b*) found that, in general, the *o*- and *m*-substituted derivatives were more reactive than their *p*-substituted counterparts and ascribed this effect to resistance of the latter compounds toward the dynamic shearing action needed for polymerization. This difference in reactivity is probably more accurately explained in terms of a static packing effect, in that the *o*- and *m*-substituted compounds should be able to pack more easily in the slipped arrangement (in which the angle, γ, between the molecular and stacking axes approaches 45°, Fig. 1) necessary for 1,4-addition without disrupting the dipolar or hydrogen-bonding interactions between molecules along the stack. Conversely, because of these intermolecular interactions, those compounds containing *p*-substituents should be forced into a much more nearly eclipsed and, therefore, less reactive configuration. We have undertaken the study of several key compounds to verify the above arguments and present the first of our results here, the crystal structure of bis(*p*-nitrophenyl)butadiyne.

The amber-tinted compound was prepared as described by Wegner (1971*b*) and recrystallized from nitromethane. A tetragonally distorted, octahedrally shaped crystal was used for data collection. One octant of data was collected on an Enraf–Nonius CAD-4 diffractometer by the θ–2θ method with Ni-filtered Cu $K\alpha$ radiation to $\theta = 78°$. The scan range was $\Delta\theta = (0{\cdot}8 + 0{\cdot}2 \tan\theta)°$ and was extended by 25% at each end of the scan range for background measurement. The scan rate was computed on the basis of a fast prescan such that 10^4 counts were to be obtained, if possible, in a maximum allowed time of 120 s. An aperture with a height of 4 mm and a variable width of $(4{\cdot}0 + 0{\cdot}9 \tan\theta)$ mm was placed in front of the scintillation counter 173 mm from the crystal. The intensities of three standard reflections, measured after every 50 reflections, varied by ~1·5% about their mean over the course of data collection. The data were corrected for Lp and background, but not for absorption.

The systematic absences $h + k + l \neq 2n$; $hk0$, $h(k) \neq 2n$; hhl, $2h + l \neq 4n$ indicated the space group to be $I4_1/amd$ (No. 141, D_{4h}^{19}) (*International Tables for X-ray Crystallography*, 1969). Of the 593 reflections measured, the intensities of 246 pairs of reflections were averaged ($hkl = khl$). The averaging residual, defined as $R = (\sum_i |F_i^2 - \overline{F_i^2}|)/\sum_i \overline{F_i^2}$, was 0·04. Of the 347 unique reflections, 55 had intensities such that $F^2 \leq 2{\cdot}5\sigma(F^2)$ and were excluded from the data set.

The structure was solved by inspection. Because of the high symmetry of both the molecule and the cell, the z coordinates of all the atoms could be readily calculated. In addition only three atoms could have non-zero x and y coordinates. Thus, the structure was easily deduced. Refinement with anisotropic temperature factors assigned to all the non-H atoms and the inclusion of the two H atoms ($B = 6{\cdot}0$ Å^2) at fixed, calculated positions converged at $R = 0{\cdot}039$ and $R_w = 0{\cdot}049$. The error in an observation of unit weight was computed to be 1·50. The change in any parameter during the last cycle of refinement was at most 0·01 of its standard deviation. The quantity minimized in the full-matrix least-squares refinement was $\sum w(|F_o| - |F_c|)^2$. The weights, w, were taken as $4F_o^2/\sigma^2(F_o^2)$. The neutral scattering factors of O, N, and C were taken from *International Tables for X-ray Crystallography* (1974). The scattering factors of H were those of Stewart, Davidson & Simpson (1965). The final atomic positional parameters are listed in Table 1.* All computations were performed with an IBM 360/195

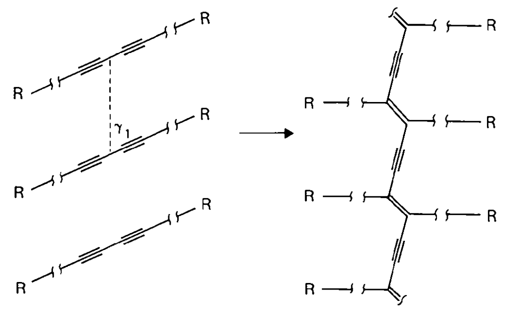

Fig. 1. The Wegner model for the solid-state polymerization of diacetylenes.

Table 1. *Final atomic fractional coordinates* (×10^4) *for bis*(*p-nitrophenyl*)*butadiyne*

	x	y	z
O	1515 (3)	0	3025 (1)
N	0	0	2810 (1)
C(1)	0	0	256 (1)
C(2)	0	0	702 (1)
C(3)	0	0	1238 (1)
C(4)	1692 (3)	0	1499 (1)
C(5)	1691 (3)	0	2013 (1)
C(6)	0	0	2260 (1)
H(4)	2874	0	1315
H(5)	2874	0	2193

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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 34282 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

computer using programs previously described (Mayerle, 1977).

Discussion. The atom-labelling scheme and the anisotropic thermal ellipsoids of bis(p-nitrophenyl)butadiyne are shown in Fig. 2. Bond distances and angles are listed in Table 2.

The four molecules in the unit cell, required to possess mm (C_{2v}) symmetry, exhibit no unusual features in their internal geometry. Thus, the C(1)—C(2) triple-bond length of 1·195 (4) Å and the C(1)—C(1′) length of 1·373 (5) Å are similar to those found in other diacetylenes (Mayerle & Flandera, 1978; Mayerle & Clarke, 1978; Hanson, 1975; Morosin & Harrah, 1977). The geometry of the p-nitrophenyl moiety also contains no unusual features. The N—O and C—N bond lengths of 1·220 (2) and 1·474 (3) Å, respectively, compare well with the values of 1·216 and 1·465 Å found in p-nitrobiphenyl (Casalone, Gavezzotti & Simonetta, 1973). In fact, even the alternation of bond lengths around the aromatic ring agrees very closely with that of p-nitrobiphenyl. Because of the symmetry, the nitro group is required to be rigorously coplanar with the phenyl ring.

The packing of the molecules within the unit cell, shown in Fig. 3, is not quite what one might have anticipated, in that dipolar interactions between NO_2 groups are absent. The packing motif is one of interpenetrating saw-tooth-like arrays of molecules running parallel to the a and b axes. The fact that the aromatic groups on either end of the molecule are mutually perpendicular allows each molecule to be a member of two such arrays.

The lack of reactivity of bis(p-nitrophenyl)butadiyne toward solid-state polymerization is trivially explained by the unexpected absence of the ladder-like stacking exhibited by most diacetylenes. Because of its high symmetry this molecule may prove to be a special case. When the phenyl substituent is larger and less symmetric, such as the various mono-substituted amino groups investigated by Wegner (1971b), more typical diacetylene packing may be observed. In this sense the present structure provides no evidence for the arguments previously proposed to explain the differences in reactivity between *para* disubstituted diphenyldiacetylenes and their *ortho* and *meta* counterparts. This result, however, does highlight the need for further structural work in this area as well as the dangers inherent in the use of solid-state packing arguments in the absence of concrete structural information.

Table 2. *Intramolecular bond distances* (Å) *and angles* (°)

C(1)—C(1′)	1·373 (5)	C(1′)—C(1)—C(2)	180
C(1)—C(2)	1·195 (4)	C(1)—C(2)—C(3)	180
C(2)—C(3)	1·436 (4)	C(2)—C(3)—C(4)	120·2 (1)
C(3)—C(4)	1·388 (3)	C(4)—C(3)—C(4′)	119·6 (3)
C(4)—C(5)	1·377 (3)	C(3)—C(4)—C(5)	120·2 (2)
C(5)—C(6)	1·369 (3)	C(4)—C(5)—C(6)	118·9 (2)
C(6)—N	1·474 (3)	C(5)—C(6)—C(5′)	122·3 (3)
N—O	1·220 (2)	C(5)—C(6)—N	118·9 (1)
		C(6)—N—O	118·3 (1)
		O—N—O′	123·5 (3)

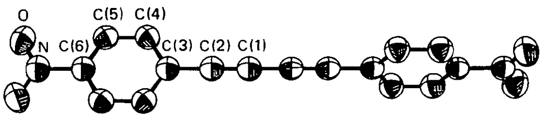

Fig. 2. The bis(p-nitrophenyl)butadiyne molecule, showing the numbering scheme and the 50% probability ellipsoids.

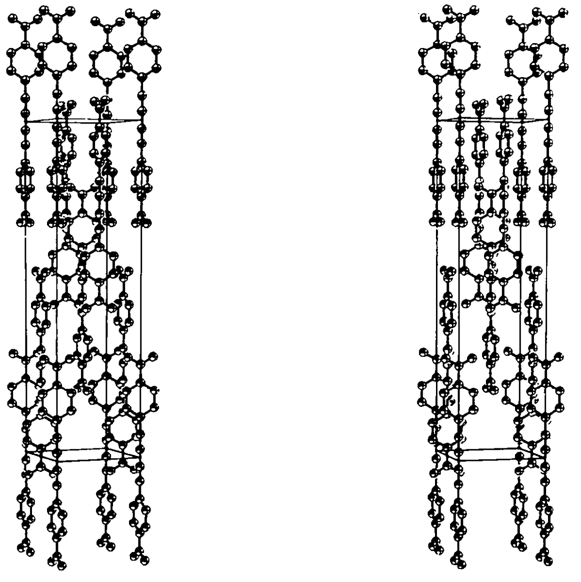

Fig. 3. The packing arrangement of the molecules. The origin of the cell is at the lower-left front corner. The a axis runs horizontally from left to right, b from front to rear, and c from bottom to top.

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