Single-crystal Study of the Solid-state Polymerisation of Butadiynylenebis-(*m*-acetamidobenzene)

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The crystal structure of the title compound is reported; a single crystal was irradiated by γ-rays and its structure determined. This reveals the presence of 20% polymer within the monomeric structure. The latter structure indicates that the side-chain causes polymerisation to be of the single crystal to single crystal type, by acting as an anchor, whereas the phenyl group rotates during reaction.

The solid-state chemistry of diacetylenes has been the focus of several recent studies, principally because of their ability to polymerise in a topochemical fashion to yield large,[1,2] high quality single crystals of polymer. At the same time there has been considerable interest in the production and performance of conducting polymers such as polyacetylene and polypyrrole, and whilst the conducting properties of undoped polydiacetylenes are generally poor, their conductivity may be enhanced by, for example, the inclusion of reducing or oxidising dopants such as I_2, SbF_5, or $AgClO_4$, or the incorporation of Cu^I ions.[3] Most diacetylenes studied so far possess side-chains which are not involved in the backbone conjugation of the polymer. Very recently, however, Nakanishi *et al.* have developed a number of diacetylene derivatives, such as the title compound butadiynylenebis-(*m*-acetamidobenzene) (DAMDP) in which the side-chain participates in the conjugation of the triple bonds in the carbon backbone.[4] A number of these, for example FDA (butadiynylenedi-[2,4-bis(trifluoromethyl)benzene] are not amenable to crystallographic study, since they react very rapidly under *X*-ray irradiation, even at temperatures as low as 100 K. Other such monomers (where side-chains are involved in backbone conjugation, for example DAMDP) react only slowly in the *X*-ray beam, but unlike FDA, they do not yield 100% polymer; reaction ceases after *ca.* 40% conversion to polymer. This is because the sample ceases to be crystalline at this degree of conversion, and thus topochemical control is lost.

In the present paper, we report the results of a crystallographic investigation of the changes in atomic parameters for DAMDP during polymerisation. This can be achieved, as it has already been demonstrated in the case of (2 + 2) cycloaddition[5–7] by determining the crystal structure of both fully and partially reacted crystals.

Experimental

DAMDP single crystals for *X*-ray crystallography were grown by slow evaporation of a dilute chloroform–methanol solution. Full intensity data were collected at room temperature on a Nicolet P3F 4-circle diffractometer with a θ–2θ scan technique, using graphite-monochromatised Cu-K_α (λ 1.541 78 Å) radiation within the limits $0 < 2\theta < 145°$. The structure was solved using direct methods and refined by full-matrix least-squares techniques. All non-hydrogen atoms were assigned anisotropic thermal parameters, and hydrogen atoms were refined isotropically.

A single crystal of DAMDP was irradiated for 134 h by γ-rays (124 Mrad; ^{60}Co source). The crystal (designated as DAMDPP) was then used for full intensity data collection, and its structure was solved using the co-ordinates of the non-hydrogen atoms in DAMDP as the starting model, with their occupancy factors allowed to vary. Significant peaks were thus located in successive Δ*F* maps, which were assigned to atoms belonging to the polymer component of the crystal. The acetamido group was refined at a single position, since separate electron-density peaks for the polymeric and monomeric components could not be located. Various methods of refinement were tried, with the most successful being blocked full-matrix least-squares,

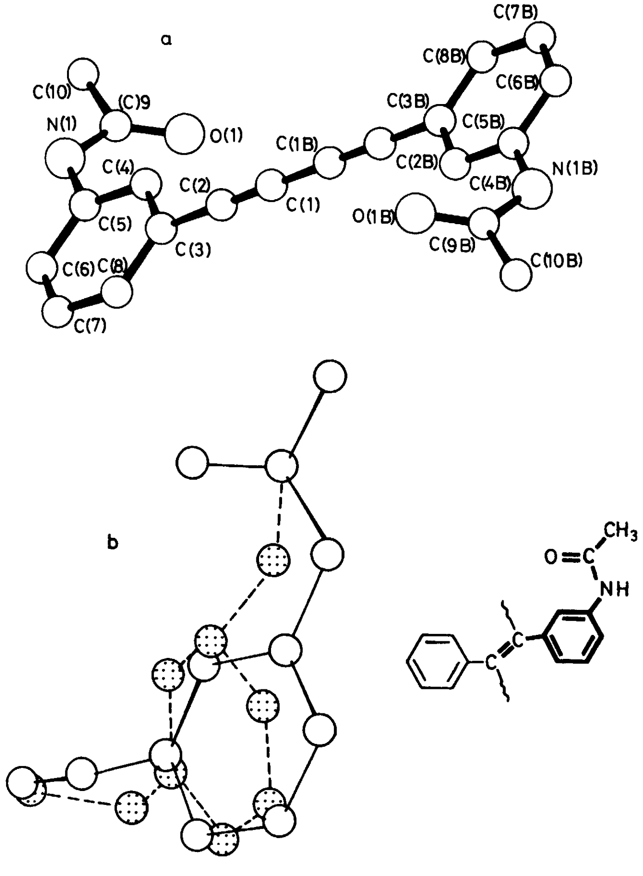

Figure 1 a, Molecular structure of DAMDP, with the numbering scheme. b, The asymmetric unit in DAMDPP: the monomeric component is shown in open circles. The polymer atoms are represented by filled circles. Note that the acetamido group is resolved at only one position

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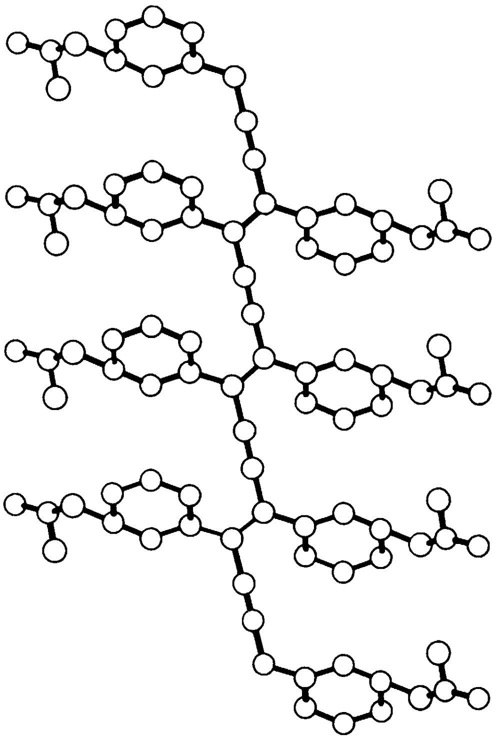

Figure 2. Fragment of the polymer chain in DAMDPP

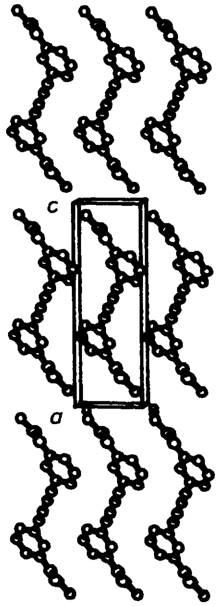

Figure 3. The crystal structure of DAMDP viewed along the a^* axis

Table 1. Crystal data

Crystal	DAMDP	DAMDPP
Formula	$C_{20}H_{16}N_2O_2$	
Mol. wt.	316.4	
D_c/g cm^{-3}	1.29	1.27
Space group	$P\bar{1}$	$P\bar{1}$
a/Å	4.859(1)	4.867(3)
b/Å	5.258(1)	5.217(4)
c/Å	16.119(2)	16.457(13)
α/Å	91.41(1)	90.97(6)
β/Å	93.62(1)	95.09(6)
γ/Å	95.64(1)	94.37(5)
V/Å^3	408.8(1)	414.8(5)
Z	1	1
F(000)	166	166
μ/cm^{-1}	5.94	5.85
Crystal size/mm	0.55 × 0.25 × 0.10	0.40 × 0.20 × 0.10
Total data	1 402	1 427
Total data observed	1 174	749
Significance test	$F_0 > 4\sigma(F)$	$F_0 > 2\sigma(F)$
Parameters	141	141
Max. peak in last ΔF map/eÅ^{-3}	0.14	0.37
Weighting scheme	Unit weights	Unit weights
Final R	0.0435	0.1660

Table 2. Atomic parameters for DAMDP ($\times 10^4$)

	x	y	z
C(1)	3 941(5)	4 550(4)	4 715(1)
C(2)	2 095(4)	3 762(4)	4 220(1)
C(3)	−119(4)	2 829(4)	3 627(1)
C(4)	−667(4)	4 249(4)	2 924(1)
C(5)	−2 854(4)	3 405(4)	2 359(1)
C(6)	−4 497(5)	1 169(4)	2 486(1)
C(7)	−3 945(5)	−243(5)	3 184(1)
C(8)	−1 755(5)	563(5)	3 747(1)
C(9)	−1 669(5)	6 153(5)	1 193(1)
C(10)	−2 852(6)	7 816(7)	542(2)
N(1)	−3 523(4)	4 894(4)	1 660(1)
O(1)	828(3)	6 015(4)	1 285(1)

the monomer and polymer contributions being refined in different blocks. Refined occupancies converged to 0.8 for the monomer, and 0.2 for the polymer contribution, well in agreement with other analyses. The monomeric non-hydrogen atoms were assigned anisotropic thermal parameters, while the other atoms were refined isotropically. Figure 1a shows the molecular structure of DAMDP, and Figure 3 the crystal packing. The asymmetric unit in both crystals is half the molecule. Table 1 contains the crystallographic details for both structures. Final atomic parameters, bond lengths and angles are presented in Tables 2 and 3 for DAMDP, and in Tables 4 and 5 for DAMDPP. Tables of anisotropic thermal parameters and of observed and calculated structure factors have been deposited as Supplementary Publication No. SUP 56642 (2 pp.).*

Discussion

The molecules are stacked with a repeat distance of 5.258 Å, with a long molecular axis inclined at 45° to the crystallographic b axis, this being a packing motif generally accepted as being conducive to topochemical polymerisation.[8] Figure 1b shows the monomeric and polymeric components in DAMDPP (one asymmetric unit only is shown), and Figure 2 the polymer chain. The C–N bond between the benzene ring and the side chain for the polymer appears to be strained. This may be due to the fact that often for polydiacetylenes the cell axis along which they stack is *ca.* 4.9 Å (*cf.* bis-*p*-tolylsulphonyldiacetylene[8]), whereas the stack axis in DAMDPP is 5.2 Å. This difference means that there is a misregistry of the polymer component in what is essentially a monomeric crystal and this is observed crystallographically as an apparent distortion in the polymer. This is also reflected in the relatively high R value achieved for this structure. A lower R value may be achieved by waiving certain restrictions imposed upon bond lengths in the polymeric components, but that

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* For details of Supplementary Publications see Instructions for Authors in *J. Chem. Soc., Perkin Trans. 2*, 1986, Issue 1.

Table 3. Bond lengths (Å) and angles (°) for DAMDP

C(2)–C(1)	1.197(3)	C(1)–C(1B)	1.374(4)
C(3)–C(2)	1.433(3)	C(4)–C(3)	1.400(3)
C(8)–C(3)	1.391(3)	C(5)–C(4)	1.385(3)
C(6)–C(5)	1.382(3)	N(1)–C(5)	1.427(2)
C(7)–C(6)	1.391(3)	C(8)–C(7)	1.380(3)
C(10)–C(9)	1.505(3)	C(9)–N(1)	1.346(3)
O(1)–C(9)	1.222(3)		
C(3)–C(2)–C(1)	179.8(1)	C(4)–C(3)–C(2)	119.3(2)
C(8)–C(3)–C(2)	121.2(2)	C(8)–C(3)–C(4)	119.6(2)
C(5)–C(4)–C(3)	119.8(2)	C(6)–C(5)–C(4)	120.4(2)
N(1)–C(5)–C(4)	120.5(2)	N(1)–C(5)–C(6)	119.1(2)
C(7)–C(6)–C(5)	119.7(2)	C(8)–C(7)–C(6)	120.5(2)
C(7)–C(8)–C(3)	120.0(2)	N(1)–C(9)–C(10)	115.7(2)
O(1)–C(9)–C(10)	120.9(2)	O(1)–C(9)–N(1)	123.4(2)
C(9)–N(1)–C(5)	125.3(2)		

Table 4. Atomic parameters for DAMDPP (× 10^4)

	x	*y*	*z*
C(1)	3 949(26)	4 602(25)	4 733(7)
C(2)	2 163(22)	3 745(26)	4 224(7)
C(3)	−83(18)	2 903(17)	3 607(5)
C(4)	−725(18)	4 290(17)	2 907(5)
C(5)	−2 949(18)	3 415(17)	2 353(5)
C(6)	−453(18)	1 154(17)	2 499(5)
C(7)	−3 889(18)	−232(17)	3 199(5)
C(8)	−1 665(18)	642(17)	3 753(5)
C(9)	−1 918(27)	6 160(20)	1 193(7)
C(10)	−2 652(33)	7 849(29)	563(8)
N(1)	−3 657(25)	4 995(20)	1 665(6)
O(1)	632(27)	5 963(25)	1 327(6)
C(1A)	3 748(38)	5 133(119)	4 921(55)
C(2A)	8 081(35)	4 559(65)	4 698(12)
C(3A)	−340(58)	3 317(52)	3 900(12)
C(4A)	319(58)	4 432(52)	3 171(12)
C(5A)	−947(58)	3 420(52)	2 428(12)
C(6A)	−2 872(58)	1 293(52)	2 416(12)
C(7A)	−3 531(58)	179(52)	3 145(12)
C(8A)	−2 265(58)	1 191(51)	3 887(12)
N(1A)	−2 246(129)	4 067(73)	1 652(26)

The indicator A for DAMDPP designates the atomic positions for the polymeric component

Table 5. Bond lengths (Å) and angles (°) for DAMDPP

C(2)–C(1)	1.207(15)	C(1)–C(1′)	1.325(23)
C(3)–C(2)	1.461(13)	C(4)–C(3)	1.395(12)
C(8)–C(3)	1.395(12)	C(5)–C(4)	1.395(11)
C(6)–C(5)	1.395(12)	N(1)–C(5)	1.445(13)
C(7)–C(6)	1.395(12)	C(8)–C(7)	1.395(11)
N(1)–C(9)	1.320(16)	O(1)–C(9)	1.254(18)
N(1A)–C(9)	1.346(42)	C(9)–C(10)	1.411(18)
C(2A)–N(1A)	1.452(29)	C(1A)–C(1A′)	1.242(48)
C(3A)–C(2A)	1.497(30)	C(2A)–C(2A′)	1.414(44)
C(4A)–C(3A)	1.395(32)	C(8A)–C(3A)	1.395(37)
C(5A)–C(4A)	1.395(30)	C(6A)–C(5A)	1.395(37)
N(1A)–C(5A)	1.431(50)	C(7A)–C(6A)	1.395(32)
C(8A)–C(7A)	1.395(30)		
C(3)–C(2)–C(1)	175.6(14)	C(4)–C(3)–C(2)	122.9(9)
C(8)–C(3)–C(2)	117.1(8)	C(8)–C(3)–C(4)	120.0(7)
C(5)–C(4)–C(3)	120.0(8)	C(6)–C(5)–C(4)	120.0(8)
N(1)–C(5)–C(4)	118.2(8)	N(1)–C(5)–C(6)	121.7(8)
C(7)–C(6)–C(5)	120.0(7)	C(8)–C(7)–C(6)	120.0(8)
C(7)–C(8)–C(3)	120.0(8)	N(1)–C(9)–C(10)	125.2(13)
O(1)–C(9)–C(10)	114.5(12)	O(1)–C(9)–N(1)	120.1(11)
N(1A)–C(9)–O(1)	86.3(28)	N(1A)–C(9)–C(10)	155.5(26)
C(9)–N(1)–C(5)	126.6(11)	C(5A)–N(1A)–C(9)	131.8(37)
C(3A)–C(2A)–C(1A)	123.4(38)	C(4A)–C(3A)–C(2A)	119.8(23)
C(8A)–C(3A)–C(2A)	119.9(20)	C(8A)–C(3A)–C(4A)	120.0(20)
C(5A)–C(4A)–C(3A)	120.0(24)	C(6A)–C(5A)–C(4A)	120.0(21)
N(1A)–C(5A)–C(4A)	144.2(28)	N(1A)–C(5A)–C(6A)	87.6(25)
C(7A)–C(6A)–C(5A)	120.0(20)	C(8A)–C(7A)–C(6A)	120.0(24)
C(7A)–C(8A)–C(3A)	120.0(21)		

Prime indicates atom outside the asymmetic unit.

would result in a chemically unreasonable structure. The restrictions relate mainly to the length of the triple and exocyclic double bonds. Removal of the polymer contributions leads to a sharp increase in *R*.

It is possible that the role of the side-chain in the solid-state polymerisation of a diacetylene is, as in the case of (2 + 2) cycloaddition, to act as an anchor, allowing the product to fit in the reacting lattice (compare for example, the case obtained in the benzylcyclopentanones[6,7,9]). For a diacetylene with a phenyl ring linked directly to the triple bond, it has been found that *meta*-substitution is more favourable towards single crystal ——→ single crystal polymerisation than *ortho* or *para* substitution. A possible explanation in purely space-filling terms is that *meta* substitution may make the side-chain more bulky, and hence a better anchor, without interfering with the movement of the reacting atoms. The anchoring effect is shown by the fact that the acetamido moiety does not move during polymerisation.

Acknowledgements

We acknowledge financial support by the S.E.R.C. and by Japan Industrial Technology Association for a visiting Fellowship to C. R. T., and we appreciate the stimulus provided by Professor J. M. Thomas.

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Received 2nd *October* 1985; *Paper* 5/1688