1972). The acridine ring system of ICR-372-OH is fairly planar with an angle of 4·2° between outer rings compared with values of 4·9° for ICR-191-OH and 10·7° for ICR-170-OH. In this system of acridine derivatives it seems that the more powerful mutagens have the flatter ring systems and better stacking of ring systems.

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Two Crystal Structures of 2,4-Hexadiynylene Dibenzoate

BY A. W. HANSON

Division of Biological Sciences, National Research Council of Canada, Ottawa, Canada K1A 0R6

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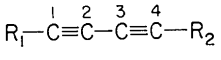
Crystals of one form ('*A*') of the title compound ($C_{20}H_{14}O_4$; F.W. 318·3) are monoclinic, $P2_1/c$, $a=14{\cdot}02$ (1), $b=4{\cdot}352$ (4), $c=15{\cdot}14$ (1) Å, $\beta=118{\cdot}9$ (1)°, $D_m=1{\cdot}306$ (2), $D_x=1{\cdot}306$ g cm^{-3}, $Z=2$. Crystals of another form ('*B*') are similar except that $a=9{\cdot}665$ (9), $b=8{\cdot}479$ (8), $c=11{\cdot}03$ (1) Å, $\beta=114{\cdot}0$ (1)°, $D_m=1{\cdot}276$ (2), $D_x=1{\cdot}280$ g cm^{-3}. The crystal structures have been determined for both forms, and refined by block-diagonal least-squares analysis of diffractometrically measured intensities. Final R indices are 0·064 (1201 observed reflexions) for A and 0·085 (1326 observed reflexions) for B. In each structure the molecule was found to have essentially the same conformation, with the hexadiyne nucleus linear and the benzoate groups approximately planar. For A (which is polymerically reactive under high pressure) the closest approach between terminal atoms of the diacetylene nuclei of adjacent molecules is 4·02 Å. For the unreactive B form, the corresponding distance is 5·37 Å.

Introduction

Many substituted diacetylenes (I) undergo solid-state



(I)

polymerization by 1:4 addition of adjacent nuclei (Wegner, 1972), while many do not; it appears that solid-state reactivity depends more on the crystal structure of the monomer than on the nature of the substituent, the latter being of importance only to the extent that it affects the former. The title compound ($R_1=R_2=-CH_2OCOC_6H_5$) is of interest because it crystallizes in two forms, one of which (A) is polymerically reactive under high pressure, while the other (B) is not (Baughman, 1972). The apparently crucial difference between the two crystal structures is that in the A form the smallest 1:4 distance for adjacent molecules is 4·02 Å, while for the B form it is 5·37 Å.

Experimental

The material crystallizes from methanol in the A form as transparent colourless prisms, elongated along **b**. The space group was determined from single-crystal photographs. The specimen used for intensity measure-

ments was $0{\cdot}45\times0{\cdot}35\times0{\cdot}20$ mm, and was mounted about **b**. The intensities of 1366 independent reflexions within the limiting sphere of $2\theta=130°$ were measured on a Picker four-circle diffractometer with graphite-monochromated Cu $K\alpha$ radiation and a scintillation-counter. The θ–2θ scan mode was used, with scans of 2° for $2\theta<100°$, and 3° otherwise. Background intensities were not measured individually, but were estimated from an experimentally determined function of θ. 165 reflexions were considered to be unobserved, as their net intensities were less than either 50 counts or 10% of the corresponding background intensity. No correction was made for absorption ($\mu=8{\cdot}8$ cm^{-1}).

The material crystallizes from diethyl ether in the *B* form as transparent colourless plates normal to **a**. The specimen used for intensity measurements was a fragment $0{\cdot}25\times0{\cdot}20\times0{\cdot}10$ mm, mounted about **b**. Experimental procedures were similar to those for *A*, except that a nickel filter was used instead of a monochromator. 1399 reflexions were measured, and of these 73 were considered to be unobserved.

Structure determination

The crystal structures were determined by the routine application of symbolic addition procedures, with all non-hydrogen atoms readily located in the *E* maps. Refinement was by block-diagonal least-squares calculations; the quantity minimized was $\sum w\Delta F^2$, where $w=w_1w_2$, with

$$w_1=4/F_o \text{ for } F_o>4$$
$$=1 \text{ (for } A\text{) and } F_o/4 \text{ (for } B\text{) otherwise, and}$$
$$w_2=2{\cdot}5\sin^2\theta \text{ for } \sin^2\theta<0{\cdot}4$$
$$=1 \text{ otherwise.}$$

These weighting schemes were found to be effective in removing systematic dependence of the weighted residual on F_o and θ. In each data set the most intense reflexions appeared to suffer from extinction. These reflexions (4 for *A*, 8 for *B*) were given zero weight. In addition, for some very weak reflexions the calculated amplitudes were found to be significantly

Table 1. *Final atomic parameters*

(*a*) Non-hydrogen atoms; quantities given are fractional coordinates $\times10^4$, $U_{ij}\times10^4$ Å^2 [T.F. $=\exp\{-2\pi^2(U_{11}a^{*2}h^2+\ldots 2U_{12}a^*b^*hk+\ldots)]\}$; e.s.d.'s are given in parentheses.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
A form									
C(1)	5222 (2)	818 (5)	4753 (2)	787 (13)	656 (12)	809 (12)	−52 (10)	495 (11)	97 (10)
C(2)	5607 (2)	2235 (5)	4331 (2)	876 (15)	674 (12)	863 (14)	−70 (11)	532 (13)	63 (11)
C(3)	6057 (3)	4093 (6)	3811 (2)	1236 (21)	662 (13)	1072 (18)	−11 (13)	791 (17)	25 (14)
O(4)	6485 (1)	2220 (4)	3295 (1)	896 (10)	744 (9)	760 (9)	9 (7)	493 (8)	−5 (8)
C(5)	7480 (2)	1059 (5)	3887 (1)	785 (12)	724 (12)	615 (10)	−24 (9)	388 (9)	−244 (11)
O(6)	7950 (2)	1431 (6)	4781 (1)	1072 (12)	1354 (16)	632 (8)	−165 (10)	444 (9)	−222 (12)
C(7)	7901 (2)	−693 (5)	3307 (1)	634 (10)	645 (11)	595 (10)	−15 (9)	335 (8)	−190 (9)
C(8)	7357 (2)	−834 (7)	2265 (2)	655 (11)	1051 (18)	619 (11)	−49 (12)	315 (9)	−49 (12)
C(9)	7806 (2)	−2452 (8)	1772 (2)	901 (16)	1269 (22)	720 (13)	−209 (14)	458 (12)	−147 (16)
C(10)	8781 (2)	−3918 (7)	2299 (2)	882 (15)	901 (17)	1119 (19)	−127 (15)	655 (15)	−118 (14)
C(11)	9322 (2)	−3801 (7)	3318 (2)	751 (14)	882 (17)	1157 (20)	153 (15)	526 (14)	33 (12)
C(12)	8890 (2)	−2196 (6)	3834 (2)	765 (13)	875 (15)	693 (12)	100 (11)	303 (11)	−130 (12)
B form									
C(1)	153 (3)	613 (4)	435 (3)	563 (14)	665 (15)	537 (13)	45 (11)	27 (11)	53 (12)
C(2)	427 (3)	1691 (4)	1199 (3)	566 (15)	705 (17)	662 (16)	3 (14)	49 (12)	61 (13)
C(3)	753 (4)	3041 (4)	2085 (4)	653 (17)	750 (20)	894 (22)	−192 (17)	19 (16)	151 (15)
O(4)	2222 (2)	2899 (2)	3179 (2)	614 (11)	615 (11)	687 (11)	−44 (9)	102 (9)	−13 (8)
C(5)	2339 (3)	1842 (3)	4130 (3)	691 (15)	588 (15)	718 (16)	−218 (13)	365 (14)	−104 (12)
O(6)	1304 (3)	1036 (3)	4078 (3)	915 (15)	997 (16)	1040 (16)	−317 (14)	526 (14)	−431 (13)
C(7)	3881 (3)	1826 (3)	5209 (3)	745 (16)	435 (12)	566 (13)	−69 (10)	325 (12)	25 (11)
C(8)	4996 (3)	2857 (3)	5219 (3)	671 (15)	533 (13)	634 (15)	16 (12)	196 (12)	0 (12)
C(9)	6415 (4)	2836 (4)	6260 (4)	625 (17)	824 (20)	832 (20)	−1 (16)	133 (15)	72 (15)
C(10)	6717 (4)	1776 (5)	7269 (3)	870 (22)	1077 (27)	658 (17)	31 (18)	174 (16)	388 (20)
C(11)	5639 (5)	722 (5)	7252 (3)	1254 (30)	964 (24)	736 (20)	325 (18)	503 (20)	496 (22)
C(12)	4212 (4)	745 (4)	6227 (3)	1056 (24)	694 (17)	789 (19)	94 (16)	558 (18)	149 (17)

(*b*) Hydrogen atoms: fractional coordinates $\times10^3$; Debye–Waller factors B. Parameters have not been refined.

	A form					*B* form			
	x	y	z	B		x	y	z	B
H(301)	662	534	427	10·0	H(301)	−4	317	242	6·0
H(302)	549	532	330	10·0	H(302)	77	404	157	6·0
H(8)	668	15	191	10·0	H(8)	477	363	449	8·0
H(9)	743	−259	106	10·0	H(9)	726	360	628	8·0
H(10)	908	−510	197	10·0	H(10)	772	176	803	8·0
H(11)	1001	−490	366	10·0	H(11)	589	−7	798	8·0
H(12)	926	−208	456	10·0	H(12)	337	−6	619	8·0

below threshold. (Such anomalies are found in many data sets, and are sometimes attributed to double, or Renninger reflexion.) Such reflexions (42 for *A*, 48 for *B*) were also given zero weight. The hydrogen atoms were assigned physically reasonable parameters, and their contributions were included in structure-factor calculations. On termination of refinement *R* (for observed reflexions only) was 0·064 for *A*, and 0·085 for *B*.* For both structures the maximum final coordinate shift was less than one quarter of the corresponding e.s.d. (which ranged from 0·002 to 0·005 Å). The final atomic parameters are given in Table 1.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30752 (15 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1 NZ, England.

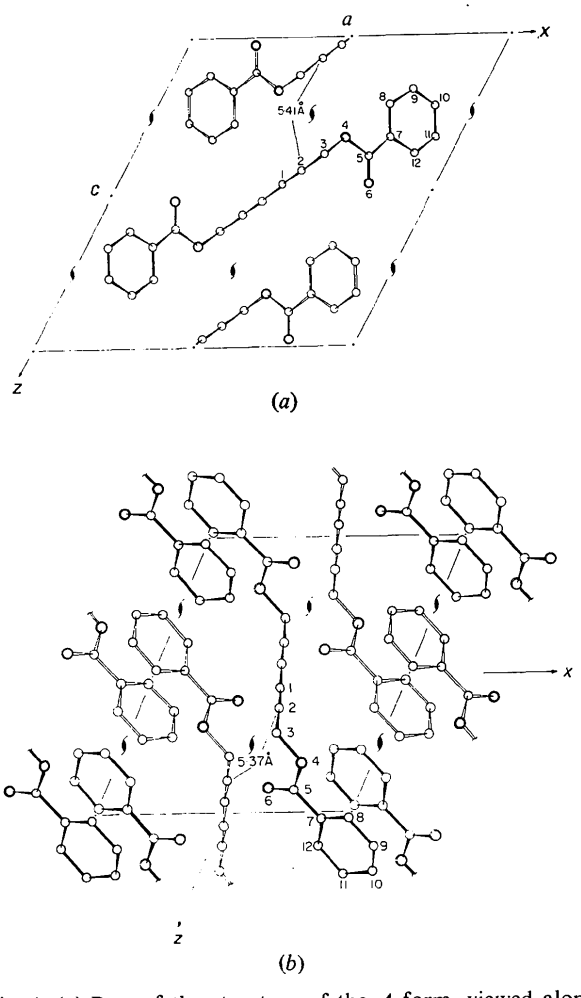


Fig. 1. (*a*) Part of the structure of the *A* form, viewed along **b**. Molecules centred at $y=0$ are distinguished by solid bonds, and those centred at $y=\frac{1}{2}$ by open bonds. A heavier outline distinguishes those atoms lying above (that is, nearer to the observer than) the centre of symmetry of the molecule. (*b*) A corresponding view of the *B* form.

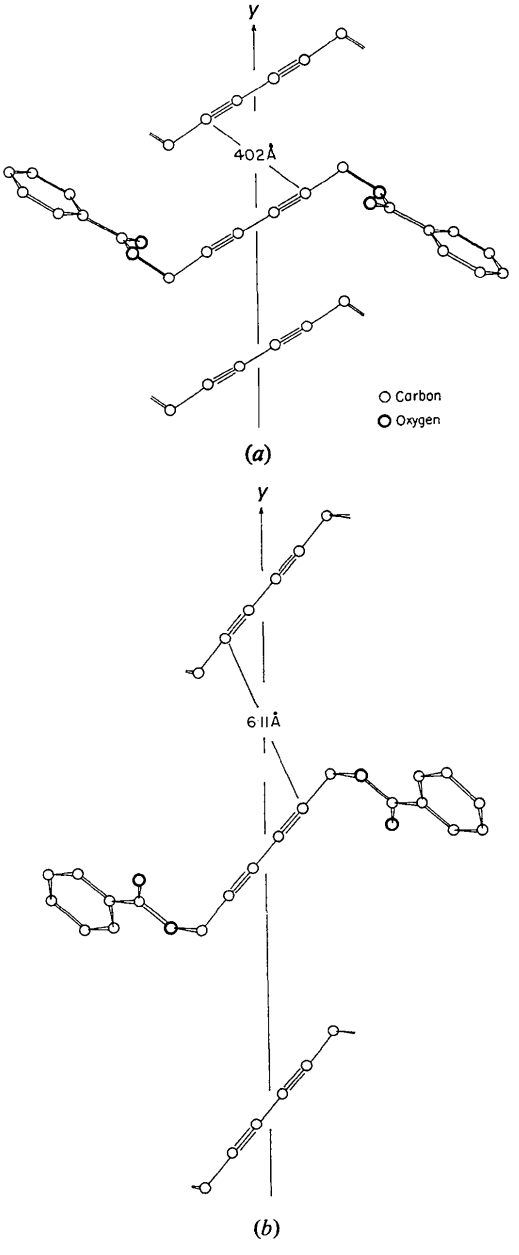


Fig. 2. (*a*) Part of one stack of the *A* form. The *b* axis and the hexadiyne nuclei lie in the plane of projection. (*b*) A corresponding view of the *B* form.

The computer programs used were those of Ahmed, Hall, Pippy & Huber (1966). Scattering factors were taken from Stewart, Davidson & Simpson (1965) for hydrogen, and from Hanson, Herman, Lea & Skillman (1964).

Discussion

The bond lengths and angles are consistent with expectation (Table 2). The hexadiyne nucleus is linear, and the benzoate groups approximately planar, although

Table 2. *Bond lengths and angles*

	A	*B*
C(1)–C(1′)	1·380 (5) Å	1·363 (6) Å
C(1)–C(2)	1·189 (4)	1·197 (4)
C(2)–C(3)	1·465 (4)	1·454 (5)
C(3)–O(4)	1·445 (4)	1·447 (4)
O(4)–C(5)	1·340 (3)	1·349 (4)
C(5)–O(6)	1·197 (3)	1·194 (4)
C(5)–C(7)	1·483 (3)	1·482 (4)
C–C (aromatic)	1·352 to 1·387	1·366 to 1·386
C(1′)–C(1)–C(2)	179·8 (3)°	179·8 (4)°
C(1)–C(2)–C(3)	177·6 (3)	177·8 (3)
C(2)–C(3)–O(4)	112·2 (3)	111·4 (3)
C(3)–O(4)–C(5)	114·9 (2)	116·6 (3)
O(4)–C(5)–O(6)	122·1 (2)	122·6 (3)
O(4)–C(5)–C(7)	112·4 (2)	111·7 (3)
O(6)–C(5)–C(7)	125·5 (2)	125·7 (3)
C(5)–C(7)–C(8)	122·7 (2)	121·7 (3)
C(5)–C(7)–C(12)	118·4 (2)	118·9 (3)
C–C–C (aromatic)	118·9 to 120·8	119·4 to 120·6

Table 3. *Distances* (Å × 10^3) *of some atoms from selected planes of the benzoate group*

Distances given in bold type distinguish the atoms used to define the plane.

Plane		Atom numbers									
		3	4	5	6	7	8	9	10	11	12
1	*A*	32	−64	31	124	**0**	**0**	**0**	**0**	**0**	**0**
	B	12	−32	35	105	**10**	**−10**	**0**	**9**	**−8**	**−1**
2	*A*	23	**−62**	**5**	**68**	**−12**	**23**	**33**	**8**	**−26**	**−39**
	B	−10	**−43**	**6**	**51**	**−4**	**3**	**26**	**19**	**−27**	**−31**
3	*A*	79	**0**	**0**	**0**	**−5**					
	B	30	**0**	**0**	**0**	**−1**					

Angle between planes 1 and 3: *A* 4·9; *B* 3·6°.

the carboxyl group is slightly twisted out of the plane (Table 3). In both structures the molecule is found in essentially the same conformation; the torsion angle about C(3)–O(4) is 79·9° for *A*, and 73·5° for *B*.

Some aspects of the crystal structures are illustrated in Figs. 1 and 2. *A* can be described as consisting of stacks of molecules extended along **b**, with the triple bonds of adjacent molecules in close proximity. The distance between C(2) and C(2′) is 4·02 Å; high pressure presumably reduces this distance to the critical value at which covalent binding occurs, with conversion of the stack to a chain. *B* is similar, but the corresponding distance in a stack is 6·11 Å, and the shortest C(2)–C(2′) distance (for molecules related by a screw diad) is 5·37 Å. Attainable pressures are apparently insufficient to reduce either distance to the critical value. The difference in polymeric activity of the two forms is thus readily (albeit trivially) explained.

The work was undertaken at the suggestion of Dr R. H. Baughman, who supplied the crystalline material and performed the density measurements.

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