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1-Acetoxy-2,4-dibromo-1,1-diphenylbutane

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Abstract. $C_{18}H_{18}O_2Br_2$, monoclinic, space group $P2_1/c$; $a = 9{\cdot}281$ (2), $b = 11{\cdot}050$ (4), $c = 18{\cdot}199$ (6) Å, $\beta = 105{\cdot}52(2)°$. $U = 1798{\cdot}3$ Å^3, $D_c = 1{\cdot}574$ g cm^{-3}, $Z = 4$, $F(000) = 848$ and μ(Mo $K\alpha$) $= 47{\cdot}8$ cm^{-1}. The structure was refined to an R value of 0·055 for 2393 reflections. The title compound is one of the products isolated in the bromination of 1,1-diphenylcyclopropylmethanol in acetic acid. Some unusual features of the proton and ^{13}C spectra can be rationalized in terms of the solid-state conformation.

Introduction. The intensities of 4624 independent reflections with 2θ(Mo $K\alpha$) $< 55°$ were collected by the $2\theta:\theta$ technique on a Syntex $P2_1$ diffractometer. 2393 reflections had intensities greater than $3\sigma(I)$ where $\sigma^2(I) = S(P + B_1 + B_2)$. Room-temperature cell dimensions were determined by a least-squares fit to 15 high-angle reflections. No absorption or extinction corrections were made. The coordinates of two Br and seven C and O atoms were obtained from an E map calculated with the *MULTAN* program package (Germain, Main & Woolfson, 1971). Least-squares refinement and Fourier techniques led to the location of all 22 nonhydrogen atoms and anisotropic refinement of the model gave an R of 0·061 where $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. All H atoms except for those on the

Table 1. *Atomic* ($\times 10^4$) *and thermal* ($\times 10^3$) *parameters*

Anisotropic thermal parameters have the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.
Parameters of hydrogen atoms were not refined.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	5859 (8)	2702 (6)	9545 (4)	49 (4)	41 (4)	32 (4)	8 (3)	12 (3)	2 (3)
C(2)	6811 (8)	1523 (7)	9629 (4)	42 (4)	46 (4)	45 (4)	8 (3)	6 (3)	1 (3)
C(3)	7067 (8)	1073 (7)	8883 (4)	50 (4)	51 (5)	45 (4)	8 (4)	16 (4)	0 (3)
C(4)	7791 (11)	−0161 (8)	8998 (5)	94 (7)	60 (5)	50 (5)	43 (5)	19 (5)	4 (4)
Br(5)	8781 (1)	1824·4 (9)	10351·6 (5)	53·9 (5)	61·9 (6)	60·8 (5)	15·1 (5)	−9·9 (4)	−7·3 (5)
Br(6)	8001 (1)	−0825·5 (9)	8043·0 (5)	70·8 (6)	72·5 (7)	57·7 (5)	20·3 (5)	6·4 (5)	−22·6 (5)
O(7)	6035 (6)	3254 (4)	10302 (3)	70 (3)	43 (3)	35 (2)	0 (3)	12 (2)	0 (2)
C(8)	5724 (11)	2600 (8)	10872 (4)	85 (6)	47 (5)	45 (5)	15 (5)	24 (4)	7 (4)
O(9)	5248 (8)	1594 (5)	10802 (3)	110 (5)	48 (4)	58 (4)	3 (4)	36 (4)	5 (4)
C(10)	6086 (15)	3348 (9)	11597 (5)	175 (11)	62 (6)	37 (4)	6 (7)	31 (6)	−10 (4)
C(11)	4178 (8)	2458 (6)	9205 (4)	46 (4)	44 (4)	39 (4)	1 (4)	17 (3)	1 (3)
C(12)	3255 (9)	3451 (8)	9122 (5)	49 (5)	58 (5)	64 (5)	12 (4)	18 (4)	4 (4)
C(13)	1710 (11)	3309 (9)	8824 (5)	62 (6)	78 (7)	77 (6)	16 (5)	25 (5)	5 (5)
C(14)	1116 (10)	2176 (11)	8594 (6)	52 (5)	106 (8)	78 (7)	2 (6)	22 (5)	7 (6)
C(15)	2054 (11)	1191 (9)	8689 (5)	68 (6)	69 (6)	67 (6)	−21 (5)	18 (5)	−8 (5)
C(16)	3574 (9)	1328 (7)	8988 (4)	51 (5)	46 (4)	53 (4)	−5 (4)	13 (4)	−1 (4)
C(17)	6451 (8)	3669 (6)	9102 (4)	45 (4)	37 (4)	41 (4)	5 (3)	15 (3)	4 (3)
C(18)	5950 (9)	3697 (7)	8307 (4)	63 (5)	46 (4)	44 (4)	3 (4)	15 (4)	4 (3)
C(19)	6559 (11)	4507 (8)	7897 (5)	90 (7)	60 (5)	48 (5)	3 (5)	23 (5)	8 (4)
C(20)	7619 (13)	5333 (9)	8263 (6)	114 (9)	67 (6)	84 (7)	−21 (6)	49 (7)	15 (6)
C(21)	8112 (11)	5328 (9)	9052 (6)	74 (7)	69 (6)	77 (7)	−20 (5)	18 (5)	−5 (5)
C(22)	7534 (10)	4493 (7)	9468 (4)	66 (6)	55 (5)	55 (5)	−11 (4)	16 (4)	3 (4)

	x	y	z	U_{iso}		x	y	z	U_{iso}
H(2)	605	086	988	3·0	H(15)	149	029	854	3·0
H(3)	775	168	868	3·0	H(16)	439	058	905	3·0
H(3′)	609	104	845	3·0	H(18)	493	305	807	3·0
H(4)	734	−081	938	3·0	H(19)	625	450	729	3·0
H(4′)	863	−046	942	3·0	H(20)	823	594	805	3·0
H(12)	378	445	938	3·0	H(21)	891	612	932	3·0
H(13)	105	416	874	3·0	H(22)	794	448	1005	3·0
H(14)	−011	229	844	3·0					

methyl group were located in a difference Fourier map. The H atom contributions to the structure factors were calculated but the parameters were not refined. The model was refined by anisotropic least-squares techniques to a final R value of 0·055 for 2393 reflections. The function minimized was $\Sigma\,\omega(F_o - F_c)^2$ where ω was set equal to 1 during the final stages of refinement. Final shifts in parameters were less than one-tenth of their estimated standard deviations. A final difference synthesis showed no peak as large as that expected for a H atom except for ripples from the Br atoms. Final coordinates are given in Table 1 while bond lengths and angles are presented in Table 2.* Fig. 1 is an *ORTEP* drawing (Johnson, 1965) projected along the C(2)–C(1) axis to show the molecular conformation and aid in the discussion of the NMR spectra.

Table 2. *Bond angles* (°) *and distances* (Å)

C(1)–C(2)	1·558 (10)	Br(6)C(4)C(3)	111·4 (4)
C(2)–C(3)	1·523 (8)	C(4)C(3)C(2)	110·0 (5)
C(3)–C(4)	1·510 (12)	C(3)C(2)C(1)	113·9 (5)
C(2)–Br(5)	1·974 (7)	C(3)C(2)Br(5)	108·1 (5)
C(4)–Br(6)	1·945 (6)	C(1)C(2)Br(5)	108·9 (4)
C(1)–O(7)	1·476 (7)	C(2)C(1)O(7)	109·6 (5)
O(7)–C(8)	1·356 (8)	C(2)C(1)C(11)	112·3 (6)
C(8)–O(9)	1·190 (11)	C(2)C(1)C(17)	111·2 (5)
C(8)–C(10)	1·518 (10)	O(7)C(1)C(17)	103·8 (5)
C(1)–C(11)	1·541 (10)	C(1)O(7)C(8)	120·0 (6)
C(11)–C(12)	1·375 (10)	O(7)C(8)O(9)	124·4 (5)
C(12)–C(13)	1·400 (12)	O(7)C(8)C(10)	109·4 (7)
C(13)–C(14)	1·386 (15)	C(10)C(8)C(9)	126·2 (6)
C(14)–C(15)	1·375 (15)	C(11)C(1)C(17)	112·3 (5)
C(15)–C(16)	1·378 (13)	C(1)C(11)C(16)	124·2 (6)
C(16)–C(11)	1·382 (10)	C(1)C(11)C(12)	116·0 (6)
C(1)–C(17)	1·527 (9)	C(11)C(12)C(13)	119·7 (7)
C(17)–C(18)	1·397 (8)	C(12)C(13)C(14)	120·1 (6)
C(18)–C(19)	1·380 (11)	C(13)C(14)C(15)	119·3 (9)
C(19)–C(20)	1·376 (14)	C(14)C(15)C(16)	120·1 (8)
C(20)–C(21)	1·386 (11)	C(15)C(16)C(11)	120·4 (8)
C(21)–C(22)	1·389 (11)	C(16)C(11)C(12)	119·8 (7)
C(22)–C(17)	1·387 (11)	C(1)C(17)C(18)	119·7 (6)
		C(1)C(17)C(22)	122·6 (5)
		C(17)C(18)C(19)	120·3 (7)
		C(18)C(19)C(20)	120·8 (7)
		C(19)C(20)C(21)	119·6 (8)
		C(20)C(21)C(22)	119·9 (9)
		C(21)C(22)C(17)	120·7 (6)
		C(22)C(17)C(18)	118·7 (6)
		C(11)C(1)O(7)	107·2 (5)

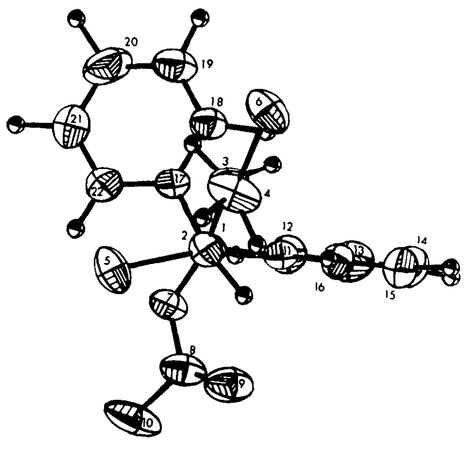
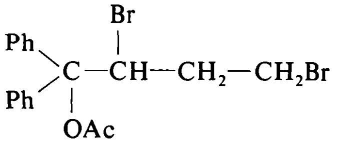


Fig. 1. A molecule of 1-acetoxy-2,4-dibromo-1,1-diphenylbutane viewed down the C(2)–C(1) bond.

Discussion. The four-carbon chain exhibits an extended conformation. The thermal motion at the C(4) end is large and the C(4)–Br(6) and C(4)–C(3) distances are more than 3σ shorter than the C(2)–Br(5) and C(1)–C(2) distances. The bond lengths were not corrected for thermal motion.



$$\mathrm{Ph_2C(OAc){-}CH(Br){-}CH_2{-}CH_2Br}$$

(I)

Although the structure of 1-acetoxy-2,4-dibromo-1,1-diphenylbutane (I) was assigned correctly, the NMR data shown in Table 3 were difficult to rationalize. The H(2) proton and the C(2) ^{13}C resonances occur unusually far downfield, and the two C(3) protons exhibit significantly different chemical shifts. Fig. 1 shows the molecular plane of one phenyl ring is oriented parallel to the C(1)–C(2) bond with the H(2) proton lying close to this plane. The carbonyl O(9) lies within 2·17 Å of H(2) and together with the ring-current effect of the phenyl group contributes to the downfield shift of H(2) to δ6·24. The interaction between H(2) and O(9) must modify the electron density

Table 3. *Magnetic resonance data*

Spectra were run in $CDCl_3$ and chemical shifts are in δ-units (p.p.m.) relative to tetramethylsilane as internal standard. Parentheses contain signal multiplicity and for the ^{1}H data the number of protons and coupling constant, J, in Hz.

C(1)	86·3 (*s*)	CH_3	2·04 (*s*, 3H)
C(2)	56·6 (*d*)	H(2)	6·24 (*dd*, 1H, J = 12 and 3Hz)
C(3)	31·2 (*t*)	H(3*a*)	1·65 (*m*, 1H)
C(4)	37·7 (*t*)	H(3*b*)	2·50 (*m*, 1H)
CH_3	22·1 (*q*)	H(4)	3·60 (*m*, 2H)
	127·0 (*d*)		
	127·5 (*d*)		
	128·1 (*d*)		
	129·1 (*d*)		
	139·6 (*s*)		
	169·0 (*s*)		

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32173 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

on C(2) which shifts the ^{13}C resonance to $\delta 56{\cdot}6$. The difference in chemical shifts for the two C(3) protons can be rationalized in terms of different average environments. From Fig. 1 it can be seen that one proton lies above the plane of the perpendicular phenyl ring while the other is in a nonmagnetic environment. The signal at $\delta 1{\cdot}65$ is consistent with an upfield shift for a proton lying above a phenyl ring. While the intramolecular interactions are weak, the sum of the interaction must be sufficient to ensure that the time-averaged solution conformation is similar to that observed in the solid.

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Trimétaphosphate de Césium Monohydraté

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Abstract. $Cs_3P_3O_9.H_2O$, triclinic; $a = 10{\cdot}610\,(6)$, $b = 7{\cdot}966\,(4)$, $c = 8{\cdot}172\,(5)$ Å, $\alpha = 96{\cdot}64\,(8)$, $\beta = 68{\cdot}84\,(8)$, $\gamma = 95{\cdot}42\,(8)$°; space group $P\bar{1}$, two formula units per cell. The crystal structure was solved from single-crystal diffractometer data by a Patterson synthesis and refined by a least-squares method. The final R value is 0·05 for 1120 independent reflexions.

Introduction. $Cs_3P_3O_9.H_2O$ a été préparé par Grenier (1973) suivant une méthode que Boullé (1938) avait appliquée au sel de calcium.

$$Ag_3P_3O_9.H_2O + 3CsCl \longrightarrow Cs_3P_3O_9.H_2O + 3AgCl.$$

Grenier (1973) a établi que $Cs_3P_3O_9.H_2O$ est triclinique et a donné une maille.

Les intensités diffractées ont été mesurées à l'aide d'un diffractomètre automatique Philips avec la radiation Ag $K\bar{\alpha}$ ($\lambda = 0{,}5608$ Å), et monochromateur en graphite. Dimensions du cristal: 0,13 × 0,15 × 0,15 mm; nombre de réflexions indépendantes mesurées: 1700; nombre de réflexions conservées pour l'affinement: 1120; domaine angulaire de mesure: $4° < \theta < 19°$; vitesse de balayage: 0,05° s^{-1}; balayage en ω; largeur: 1,2°(θ).

Une sommation de Patterson tridimensionnelle a permis de localiser les atomes de césium dans l'hypothèse du groupe $P\bar{1}$. Des sommations de Fourier révèlent les atomes de phosphore et d'oxygène. La molécule d'eau apparaît sur une synthèse de Fourier différence. L'affinement du modèle obtenu dans le groupe $P\bar{1}$, par une méthode de moindres carrés, effectué au moyen du programme *SFLS*-5 de Prewitt (1966) sur 1120 réflexions conduit à une valeur de $R = 5\%$.* Les

Tableau 1. *Coordonnées cristallographiques des atomes*

	x	y	z	B
Cs(1)	0,0133 (1)	0,2592 (2)	0,2598 (2)	2,34 (2)
Cs(2)	0,6233 (1)	0,1225 (2)	0,1955 (2)	2,43 (2)
Cs(3)	0,6587 (1)	0,3796 (2)	0,7219 (2)	2,35 (2)
P(1)	−0,0029 (5)	0,2412 (6)	0,7732 (7)	1,72 (5)
P(2)	0,2479 (6)	0,4223 (6)	0,7710 (7)	1,79 (5)
P(3)	0,2570 (5)	0,1374 (6)	0,5121 (7)	1,47 (5)
O(*L*1)	0,323 (2)	0,257 (2)	0,645 (2)	2,8 (1)
O(*L*2)	0,100 (1)	0,109 (1)	0,634 (2)	2,1 (1)
O(*L*3)	0,097 (2)	0,349 (2)	0,861 (2)	2,8 (1)
O(*E*11)	−0,049 (1)	0,359 (2)	0,674 (2)	2,6 (1)
O(*E*12)	−0,099 (2)	0,141 (2)	0,906 (2)	3,0 (1)
O(*E*21)	0,311 (1)	0,453 (2)	0,909 (2)	2,9 (1)
O(*E*22)	0,256 (2)	0,557 (2)	0,660 (2)	2,8 (1)
O(*E*31)	0,268 (2)	0,235 (2)	0,367 (2)	3,2 (1)
O(*E*32)	0,325 (1)	−0,023 (2)	0,476 (2)	2,9 (1)
H_2O	0,413 (1)	0,206 (2)	0,018 (2)	2,6 (1)

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* La liste des facteurs de structure a été déposée au dépôt d'archives de la British Library Lending Division (Supplementary Publication No. SUP 32172: 9 pp.). On peut en obtenir des copies en s'adressant à: The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, Angleterre.