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Neutron-Diffraction Refinement of the Crystal Structure of 1,3,5-Triacetylbenzene

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A neutron-diffraction investigation of the crystal structure of 1,3,5-triacetylbenzene has been performed in parallel with an X-ray diffraction analysis, as part of a study of electron-density distribution. Data were collected with two crystals at a neutron wavelength of 1·192 Å, the total number of 1576 independent reflexions being limited to a maximum of 0·57 Å⁻¹ in sin θ/λ . The positional and anisotropic thermal parameters were refined by block-diagonal least-squares calculations on $|F|^2$ with allowance for extinction effects in the data. The final model is discussed with reference to the intra- and intermolecular geometry and thermal motion.

Introduction

The present investigation (here abbreviated TABN) of the crystal structure of 1,3,5-triacetylbenzene (TAB) has been performed to complement the X-ray study (TABX) of TAB described in the accompanying paper by O'Connor (1973). Combined X-ray and neutron diffraction studies of organic molecules have been used, for example, by Coppens (1967), Coppens, Sabine, Delaplane & Ibers (1969) and Coppens & Vos (1971) to investigate the nature of the charge-density distribution in, respectively, sym-triazine, oxalic acid dihydrate and cyanuric acid. The advantage of using combined analyses for this purpose is that positional and thermal parameters obtained with neutron parameters can thus be employed with the X-ray data to construct Fourier difference maps which ideally reflect only the inadequacies of the spherical atom approximation (see TABX). If the expected bonding features are evident in the difference maps, it is then most useful to attempt a least-squares study of the valence-electron distribution, in which the positional and thermal parameters are fixed at the neutron values.

The details of molecular geometry and thermal motion are discussed in this paper rather than in the TABX account because of the general superiority of the neutron parameters.

Experimental

The sample of TAB which had been used to grow crystals for the TABX study was purified further by successive recrystallizations from acetone. It was then a simple matter to obtain crystals of sufficient volume for neutron diffraction by seeding a saturated solution of TAB in acetone. The crystals were all monoclinic prismatic with development of the $\{100\}$, $\{010\}$ and $\{001\}$ faces and were characterized by preferential growth normal to the unique axis. The intensity data were recorded with two crystals, the dimensions of which are given in Table 1. The smaller specimen (crystal 1) was used to measure the low-angle reflexions

Table 1. Crystal dimensions					
Face indices	D*(Crystal 1)	D*(Crystal 2)			
$\left.\begin{array}{cc}1&0&0\\\overline{1}&0&0\end{array}\right\}$	0·040 cm	0·120 cm			
$\left. \begin{array}{c} 0 & 1 & 0 \\ 0 & \overline{1} & 0 \end{array} \right\}$	0.224	0.480			
$\left[\begin{array}{c} 0 & 0 & 1 \\ 0 & 0 & 1 \end{array} \right]$	0.470	0.762			

* Length of normal between the specified pair of faces.

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with the intention of reducing extinction effects and the larger specimen (crystal 2) was used for the high-angle reflexions in order to maintain an acceptable level of counting efficiency for the full range of data considered.

The intensity profiles were measured with a manual three-circle diffractometer situated at port 4H5 of the reactor HIFAR which is operated at Lucas Heights by the Australian Atomic Energy Commission. The incident neutron beam, obtained by reflexion from the (111) planes of a copper crystal monochromator, had a measured wavelength of 1.192 Å and a flux of approximately 5×10^5 neutrons cm⁻² s⁻¹. The profiles were recorded by the $\theta/2\theta$ -scan technique in the 'symmetric' instrument configuration, with the detector being stepped in increments of 3' over a range of 5° divided equally between the peak and background segments of the profile. Careful analysis of the profile maxima showed that the $P2_1/c$ cell parameters from the TABX study [a=8.386 (3), b=16.333 (5), c=7.644 (3) Å; $\beta = 93.69$ (3)°] were acceptable within the setting precision of the diffractometer circles. These cell parameters were adopted throughout the course of the TABN investigation.

468 acceptable reflexions were recorded with crystal 1 in the low-angle range of reciprocal space defined by the upper limit 0.420 Å⁻¹ in sin θ/λ , and a further 1352 were recorded with crystal 2 in the range $0.300 \le$ $\sin \theta / \lambda \le 0.570$. As the goniometer angles and initial detector position for the profile scan were set manually, it was necessary to devise checking procedures which indicated with reasonable certainty those reflexions that had been mis-set. It was not feasible, however, to assess the reliability of setting at the time of measurement. During the subsequent data-reduction stage, by which time the diffractometer was no longer available, 94 of the total 562 accessible in the low-angle range were rejected on the grounds that the angular settings were possibly in error. For the same reason 97 of the total 1213 accessible in the high-angle range were rejected. The list of 1352 acceptable high-angle data includes 244 reflexions also present in the set of lowangle data. These duplicate measurements were not averaged as part of a merge procedure as it could not be assumed that the extinction parameters for the two crystals would be identical. The structural least-squares refinement was therefore performed with two unscaled lists of data, the total number of independent observations for this purpose being 1576.

The reflexions 204 and $25\overline{2}$ were measured twice daily as standards during the data collection. Results showed that the counting system was effectively stable during the experiment. The intensity profiles were reduced to estimates of intensity by dividing each profile into peak and background sections such that the number of points in each section of background was the same, and together equalled the number of peak points. The intensity for *P* counts on the peak and *B* on the background is then

$$I = P - B$$

The estimates of variance were determined with the approximation

$$\sigma^2(I) \simeq \sigma_1^2(I) + pI^2$$

where $\sigma_1^2(I) = P + B$ is the contribution from counting statistics. A reasonable estimate for p in the term pI^2 . which is included to account for instrumental missetting errors, was not available at the data-reduction stage so that only the $\sigma_1^2(I)$ could be formed then. Absorption corrections were calculated according to the procedure of Busing & Levy (1957). The value of the linear absorption coefficient used in these calculations, 2.45 (10) cm⁻¹, was determined in a simple transmission experiment on crystal 2 with the detector mounted in the straight-through position. It is of interest that the experimental value for the absorption coefficient corresponds to a mean total scattering cross-section of 47 barns for hydrogen in TAB, compared with the value of 20.36 barns quoted by Melkonian (1949) for hydrogen in the free state. Note that the experimental proton scattering cross-sections (given by Melkonian for the neutron energy 0.058 eV used in the TAB determination) are 39, 42 and 44 barns for liquid state H_2O_1 , n-butane and cetane, respectively.

The final lists of F_o^2 and $\sigma_1^2(F_o^2)$ for the two crystals are presented in Tables 2 and 3.

Table 2. Observed structure factor squares (FOSQ) forcrystal 1 with the estimated standard deviations (ESD)based on counting statistics

	H & 1(CONT)	# # 11C1NT;	H & 21CONTS	# # 3(CONT)	H # 4(CONT)
· · · · · · · ·	 L F350 (50 	A L FUSU ESC	# L FUSH (S)	8 L F054 F50	E . 6351 (S)
• 254 22	1 4 27 74	14 -4 370 74	0 -3 40 89	3 -5 84 187	3 -1 116 97
1 025 34	/ - A 389 70	.18 -3 -130 6:	6 -2 15: 83	3 -4 472 183	3 0 975 189
	110 12	:	6 -1 2136 134	3 -3 110 90	3 1 225 97
		10 11 11 11	v a -57 55	3 -2 22/1 11/	3 2 153 182
5 . 5 4 97			0 1 1011 05	3 -1 -30 75	3 3 -70 102
6 124 70	-1 140 44				3 4 158 118
6 11575 57	· 1 275 Ac	11 -1 2034 145	6 4 19- 93	1 2 27 86	
5-3	. 4 .17 68	12 0 38- 101		3 3 18, 95	4 -2 -143 90
2 N. S.	1-11 11e	11 1 34, 54	7 - 5 - 20 7	3 + SP; 10v	4 -1 4391 193
5 2 4 7 5 5 C 4		11 2 332 145		3 5 30 73	4 8 500 90
		11 3 2764 116		4 - 5 3/ 72	5 -4 778 110
6	1		2 2010 114	4 - 4 Jan 30	5 -3 -65 95
1 4- 4.		12 3 223 162	7 1 1414 111		2 - 2 V8 V9
2 9-1-144	سه وم ارد ه	17 1 2825 93	2	4 10 144 12	
1 445- 211	1 -1 17-6 15	17 7 102 112	7 % 300 úd	4 3.50 100	5 1 .50 114
	5 7 37411 154	10 11 372 74	7 4 340 95	4 2 857 94	5 2 1+70 129
	1 1 1 1		5 - 5 - 5 - 5 - 5 - 5 - 5 - 5 - 5 - 5 -	4 3 11 41	5 3 ;72 10a
22 54			2554 144	16, 196	6 -3 162 168
2.5: **	22.2	 F.S. 15. 			0 -1 1284 111
5 . 4, 90	5 775 74	6 -4 2114 11	A 1 -4/ A5	4 - 3 72 1 4 3	0 1 -191 91
• -:21 e4	5 A -110 7s	P - 2 - 2 - 4 - 4 -	8 2 1815 185		0 4 1134 115
		# # 10520 125			6 3 750 114
		· · · · · · · · · · · · · · · · · · ·	1 1	5 1 744 94	7 -3 3005 103
		1	· · · · · · · · · · · ·	2 6 2/2 120	7 - 2 1023 112
1 2514 115	4 -1 1/14 24	1 -2 3267 164	9 . 2 . 5		-) e74 186
• • •	1 1 1 1 1 1 1 1	1 4 1 6 44			7 6 8451 199
2, 2020, 232		1 - 3 362 91	9 1 67/ 98	6 -3 15. 90	7 2 421 105
	• • • • •	1 -2 +0, 71	0 3 240 99	e -2 157/113	8 -1 754 198
		1 -1 /20	· · /11 //	e -1 -1,4 83	A 5 454 185
1 14 135	· · · · · ·	1 2 40 24			P 1 1/56 111
• • • • • • •	+ · · · · · · · · · · · · · · · · ·	1 1 11/2 11/2	4 -2 343 97	6 2 6 A	
5 1121 114	5 -1 -16 A1	1 4 1490 131	10 -1 -41 110	0 1 /01 90	9 1 229 94
		3 5 50 200	:4 3 -13 67	e e 68' es	
		2 -0 404 01	11 -3 -10 05	7 - 3 1/ 41	~ • • •
		2	11 -2 11/ 63	**? 3610 141	
21 67					1 1050 [53
0 2417 95	- 1 -5 81	6 -2 412 71	11 1 1041 154	2 2 4511 175	
1 1 6 7 27	· · · · · · · · ·	r -1 740 Ar	11 2 11 05	7 3 764 105	4 4 401 3 102
5 5.45 114	5 5 718 111	e e 🔹 34	11 3 1190 83	8 -2 1044 110	1 -3 376 187
	100 01	4.3 57	12 -2 -46 42	· -1 2-0+ 133	1 -2 782 184
			12 11 214 74	20: 95	1 -1 3531 14>
41, BA	1 4 2 11		12 1 107 20	· · · · · · · · · · · · · · · · · · ·	1 8 783 187
3 1136 116	1.40 0.	3	2 2 740 80	1 1133 111	1 1 110 125
e - 1-14 - 194	· · · · ·	3 -5 264 42	11 -1 1174 49	9-3 0 ¥e	2 -3 571 185
1 1 1 1 1 1 1 1		3 -4 43:1 143	13 # 65/ 75	9 - 2 224 92	2 -2 1512 120
		3 - 5 444 44		5 -1 157e 115	2 0 1570 125
		1 1 1 1 1 1 1	H + 3		2 2 241 185
1. 100 110	1		K 1 5150 75	0 2 205 0h	× > 161/13>
	· · · · · · · · · · · · · · · · · · ·	3 1 47, 41	4 +4 2724 145	1	3 -2 2384 137
5 2 3. 3-	5 - 1 - - 1 - 5 - 5 -	3 2 3730 115	0 -2 5240 143	18 -1 164 90	3 -1 1041 119
	r a 188 15	3 3 1483 147	P P 52 33	18 0 572 183	3 8 2525 141
		3 6 6 1 1 1	8676 187	14 1 00 9.	3 2 351 111
2-1					-3 3177 163
5.20		4 - 1 - 4- 00	1 -4 1175 124		1 1078 135
	· N 17 Ac	4 -2 3324 An	1 -3 0174 177	* L FLS_ ES.	4 1 1417 126
• • :	· · · · · · · · ·	4 -1 015 70	1 -2 71 85	P -4 740 111	4 2 57 185
1 4	- 2,60		1 -1 1/52 1/42	4 4 4887 146	5 -7 1364 124
1.01.0		100	1 1 1 1 1	6 2 0. 00	5 -1 034 115
1.4.	345 5	4 1 6414 10	1 2 294 64	1 -7 34-6 138	- J 442 184
a	425 4		3 3 3 1 1 1 1 1		5 2 111 144
1-43-214	n 2 100 m	5 . 5 300 4-	4 1 5 22	1 2 2315 125	0 -2 5437 :03
-: 61 75	4 1 2311 114	5 -4 - 524 133	3 3 1023 125	1 3 4 36	6 -1 43:4 175
	2 4		2 -	1 4 101 144	6 4 942 117
			2 - 4 3.4 18 1	3230 154	-1 0001 :95
	1 15 - 41		2 .2 2.41	2	· • ••1 185
14 42	Sec. 3283 111	5 2 1 1 M	2 -: 1494 41	2 444 1 14-	•
2+9- 0-	10 An	- 1	2 1 115 42	2 3 50+ 110	
5194 91	 - 1, - 4, - 111 	5 4 185 95	2 1 245 82	7 4 254 110	 U FUSS ESC
11 21	1 112 122	2 2 2 2	2 2 310 97	3 -4 1221 134	2 . 2 90 90
44.51 3.25			2 4 636 18.	3 - 3 1 3 3 1 9 6	P P 194 162
,		· · · · · · · · · · · · · · · · · · ·	2 4 61 184	1 - 2 - 615 - 11	1 - 2 71 163

Structure refinement

The model from the TABX analysis was refined by block-diagonal least-squares minimization of the quantity $\sum_{i} \sum_{\mathbf{H}} \tilde{w}_{i}(\mathbf{H}) \cdot [F_{oi}^{2}(\mathbf{H}) - F_{c}^{2}(\mathbf{H})y_{i}(\mathbf{H})/k_{i}]^{2}$ where $\dot{y}_{i}(\mathbf{H})$ is the extinction factor for reflexions H in the *i*th data list. The mosaicity model adopted for the determination of y_i was the isotropic model described by Zachariasen (1969), in which the crystal is represented as an aggregate of perfect spherical domains of radius r_i with the misorientation of the domains following an isotropic Gaussian distribution of the form

$$W_i(\Delta) = \sqrt{2g_i} \exp\left(-2\pi g_i^2 \Delta^2\right).$$

In this approximation the extinction factor is

$$y_i(\mathbf{H}) = [1 + 2Q_i(\mathbf{H})T_i(\mathbf{H})r_i^*/\lambda]^{-1/2}$$

Table 3. Observed structure factor squares (FOSQ) for crystal 2 with the estimated standard deviations (ESD) based on counting statistics

T٤	ıbl	le	3	(cont.)
				`	

н т	+11.34	•	H 1 4100%")	H C 51, MIL	4 1 6(1347)	H # 7(2061)	
ι,	USU E	5,	· L FUSUISU	A & FUSU (SU	K . F.S. (S)	5 . Fu5. 155	A
1 1	r 81	50	17 e 45 24	0 1 237 15	1 1 610 30	1 -5 554 61	8 -2 452 3
44	127	5.	17 1 10 24	0 3 187 14	\$ 2 3520 54	3 - 4 457 35	0 8 571 J
	3.	33	17 1 130 24	0 4 61 13	3 4 170 14	1 -2 64 31	
;	134	30	14 -1 14 20	0 0 107 44	1 6 - 10 10	1 6 124 23	1 -5 43 5
-? ?	.80	•••	10 4 152 24	V . 6 157 50	4 - 6 3 34	1 1 - 30 30	1 -3 455 6
-5 6	400	;;	11 2 213 43	V - S - SA 4/	4 - 4 11 23 41	1 2 215 33	1 -2 878 3
	122	22		¥ =3 1360 44	4 -3 2599 44	1 4 140 50	1 1 1648 4
-3	795	**		V -2 1327 42 V -1 1476 41	4 - 2 2725 42	1 5 77 59	: 2 307 0
-1 1	580	,,	 E. E.S. ES. 	V 10 620 50	4 4 6 57	2 -5 681 64	1 4 -54 5
1	- 6 3	5H 40	· · · · · · · · · · · · · · · · · · ·		4 1 65 35	7 -4 1167 41	2 -5 188 5
÷ i	127	00	· · · 3140 70	v 3 14, 14	4 3 743 45	2 -2 564 35	2 -3 392 6
4	*2*	:	7 4 643 (n 1 6 447 5)	V 4 -57 34	4 4 112 37	2 -1 455 34	2 -2 108 3
•	190	34	: -7 1/40 1/	30 34 40	4 6 -14 67	2 1 17 24	2 8 06 3
;	1	12	1 - 1 142 14	10 - 5 15 47	5 -6 113 64	2 2 94 32	2 1 4 3
- /	- 23	31	1 -4 14 14	0 -3 2117 40	5 4 414 30	2 4 533 65	3 3 35 5
	145	37		18 - 790 30	5 - 3 372 37	2 5 2/ 50	2 4 34 5
-4 1	e 6 7	••	1 -1 3/25 24	30 6 84 13	5 -1 2554 50	3 - 5 , 2+ 54	3 .4 201 0
-1 -1	629	55	1 1 1 1 2 2	10 1 1021 41	5 8 3414 53	3 -4 421 42	3 - 3 150 5
ý,	160	91	1 2 -14 13	28 3 383 54	5 2 580 16	3 - 2 484 34	3 -1 518 3
2	283	54	1 5 439 19	10 7 140 44	5 4 30 35	3 -1 767 37	3 8 877 3
ŝ	45.2	30	1 0 14 13	11 - 5 : 6 45	5 5 44 67	5 1 247 34	3 2 52 6
2	510	51		11 -1 -1 14	5 6 -30 63	3 3 274 36	3 3 112 0
-?	55	31	× -6 124 35	11 - 2 30 34	6 -5 52 63	3 5 13 60	4 - 4 212 5
	415	20	2 - 5 82 13	11 1 21 11	6 -4 613 41 6 -2 -6 14	4 -6 188 58	4 - 3 586 6
- 1	1991	55	/ -5 444 20	11 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	0 -1 28441 182	4 - 4 133 34	4 -1 -56 3
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i.	513	55	1 1 2221 21	11 5 -10 4/	6 4 278 41	4 -1 2490 50	4 2 -18 6
1, 1	109/	50	2 374 24	14 - 5 150 40	7 -0 20 65	4 8 1874 48	4 3 676 6
3	137	55	2 4 492 37	32 -3 444 40	7 -4 414 40	4 2 54 34	5 . 5 457 6
:	391	34	2 5 -17 sn	1/ -/ /30 15	7 -3 4435 65	4 3 668 48	5 -2 300 0
÷	24	27	1 7 25 31	12 0 145 35	7 -1 2112 30	4 5 61 61	5 8 347 3
- 1	334	40	1 -7 479 35	14 1 2400 41	2 1	5 -5 340 63	2 1 387 0
- 5	14	21	5 -5 1042 41	17 3 730 44	2 4 127 73	5 -3 1374 43	5 3 70 6
-2		30	1 -4 16# 33	14 4 245 44	2 5 20 72	5 -7 756 30	6 - 4 19 2
ĩ	44	4,	3 -1 2640 71	13 -3 14 44	8 -5 424 71	5 8 1828 43	6-2 74 5
÷.	184	21	5 - 1 447 67	13 -7 487 47	8 . 4 824 43	5 1 16 35	0 -1 382 0
•	- 31	31	5 1 AS 10	13 4 305 30	8 - 2 7494 70	5 4 401 00	0 1 -14 0
•	130	34	3 3 90 14	13 1 1025 5/	8 -1 1050 45	5 5 164 65	6 2 384 6
÷,	142	14	3 5 -23 17	13 2 433 46	6 1 110 16	6 - 4 - 37 68	7 - 3 1295 7
- 5		35	5 6 -4 44	14 - 3 11 44	8 2 1585 45	6 -3 622 39	7 - 2 - 1 - 2
	27	30	4 -6 641 44	14 -1 887 50	8 4 29 65	6 -1 435 30	7 8 87 4
- ?	44	30	4 -5 3195 57	14 8 105 46	4 5 62 64	6 8 -74 36	7 1 1011 5
-1 1	245	30	4 -/ 300 61	14 2 -17 4/	9 -4 627 75	6 2 225v 54	7 3 1949 8
i	103	30	4 -1 1749 74	14 3 687 40	9 -3 265 39	b 3 4v80 113	8 -3 495 6
2	524	34		15 -2 140 34	9 -1 410 43	7 - 5 324 60	5 -1 142 6
	42	33	4 5 58 54	27 8 43 34	0 3 -4 36	7 - 3 - 24 54	6 8 -24 S
à	- 11	31	4 4 93 69	17 1 10 34	18 - 5 - 14 71	7 -1 4131 61	8 2 67 7
- 0	184	32	4 6 3Ad 54		10 -4 20 67	7 8 1591 48	9 - 2 - 4 - 5
	-16	30		нта	18 -2 344 12	7 7 1500 49	9 8 284 0
-3 2	517	47	5 -5 1541 57	R L FUSUESU	18 -1 2442 55	7 4 284 64	9 1 79 6
-?	377	34	4 - 15 20	P - 4 21 8 32	18 1 426 34	8 - 4 - 50 01	18 8 417 6
	137	34	5 -1 1107 70	0 -2 -30 51	18 2 -24 19	8 -3 384 69	
3	380	31		8 4 2574 51	10 4 5 70	8 -1 39 37	
3	-14	31	5 2 14 40	· · · · · ·	11 -4 210 24	A # 2420 54	L F050 Ex
;	-22	30	5 4 171 3/	1 -0 -40 5-	11 -2 53 55	8 2 1942 93	0 0 234 4
- 5	- 4 5	24	5 1A 1A	1 -5 2560 47	11 -1 664 41	8 3 644 77	
	113	34	2 0 310 V 2 162 51	1 - 3 11 24	11 1 292 35	0 -4 05 03	1 -2 53 5
-2		31	a a - a - a - a - a - a - a - a - a - a	1 - 2 22 23	11 2 191 79	9 -3 22 62	1 -1 344 5
-1	043		7 -4 416 34		11 4 185 65	9 -1 00 30	1 1 2208 0
	305	11	· · · · · · · · · · · · · · · · · · ·	1 1 343/ 0/	12 -4 -45 89	9 8 0 30 9 1 333 72	1 2 -10 2
ŝ	117	34	n -1 3541 AD	1 3 10/ 1/	12 - 2 - 6 6 5	9 2 82 67	2 - 2 - 82 5
	330	31	8 -52 A4	1 4 200 10	12 -1 154 46	9 3 113 65	2 -1 55 5
	50	3+	n 2 613 32	6 4 30	12 1 151 65	18 -3 -14 02	2 1 15 5
-	-1	2	A 4 686 3V	2 -7 640 ^5	12 2 -61 63	18 -7 411 07	3 - 3 - 14 5
	20	33	A A 25 47	2 - 5 - 5 - 54	3 - 2 35 63	10 0 730 75	3 - 2 033 0
-1	114	30	7 - 6 117 50	2 2 2	13 M 18 AP	18 1 574 73	3 -1 40 2
1 2	120	33	/ 1/03 46	2 - 2 11**	15 2 576 74	10 3 214 70	3 1 334 6
2.1	5194	51	/ -3 341 40	2 -1 -05 55	14 -2 214 65	11 -3 -16 64	3 2 171 3
3	5	20	1 -1 5405 90	1 700 AS	14 4 343 66	11 -1 51 67	
- 4	5.0	24	/ 1 1502 51	2 2 94 32	14 1 740 72	11 8 -53 87	121
-3	304	31	/ 3 -10 15	2 4 495 34	н + 7	11 2 327 71	5 - 2 - 11 - 5
-1 1	185	40	1 4	<pre> * ? ? ?</pre>	R 1 F150 - 51	17 -7 44 65	5 1 100 5
í	157	34	A 7 A 50	3 - 6 - 50 3-	8 -0 210 55	12 0 0 00	5 1 330 5
	24	2.		3 - 3 1425 20	8 -4 19 12 8 -2 1439 43	17 1 68 69	6 -1 28 5 6 8 241 A
4	-20	20	3 3973 50	3 -3 1004 14	8 8 727 70		
- 3	170	34	4153 54	3 -2 -54 - 34	A 2 120 31	# 1 705u 150	
-1	-21	21	e - 1 - 1 - 1 - 1 - 1	3 -1 1787 00	1 0 137 50	8 -4 171 57	

where

 $Q_i(\mathbf{H}) = F_c^2(\mathbf{H})\lambda^3/V_c^2 \sin 2\theta$ for neutron diffraction, $T_i(\mathbf{H})$ is the mean path length for reflexion \mathbf{H} ,

and

$$r_i^* = r_i / [1 + (r_i / \lambda g_i)^2]^{1/2}$$

is the extinction parameter to be refined in the leastsquares calculation. The undefined symbols have their usual meaning.

In the block-diagonal calculation the following block structure was adopted: 9×9 matrices for each of the 27 atoms in the molecule (i.e. each atom was treated as anisotropic) and a 5×5 matrix for the parameters k_1, k_2, r_1^*, r_2^* , and the customary 'artificial' isotropic thermal parameter. The scattering lengths for carbon, oxygen and hydrogen were fixed at 6.61, 5.77 and -3.78f (Bacon, 1962), respectively. All reflexions were included at the measured value of $|F_o|^2$ including those with small negative values. In the preliminary refinement the least-squares weights were set at $1/\sigma_1^2(F_o^2)$ since the constant p was not known in advance. This weighting scheme placed too much emphasis on the strong reflexions, to the extent that the calculation diverged when the full parameter shifts were applied. Suitable acceleration factors (0.25 for positional parameters and 0.20 for thermal, scale and extinction parameters) were arrived at by trial and error. Then cycles of least-squares calculations reduced the residuals* R(F) and $R(F^2)$ to 0.098 and 0.088, respectively, and the 'goodness-of-fit' index* G to 1.91.

The least-squares calculations were then continued with estimated absolute weighting factors, the constant *p* being determined from the results of an analysis of structure-factor agreement in the manner described in the TABX paper. This gave a value of 0.0043 for *p*. Six cycles of refinement, full shifts being applied, were performed with the absolute weights, and these reduced all parameter shifts to insignificant values. The final residuals were 0.093 and 0.087, and the final *G* index was 1.12. The extinction parameters r_1^* and r_2^* were 0.145 (39) × 10⁻⁴ cm and 0.100 (13) × 10⁻⁴ cm, respectively.

The positional and thermal parameters for the refined model are listed in Table 4.

*
$$R(F) = \sum_{i=1}^{n} (F_o - F_c) / \sum_{i=1}^{n} F_o, \ R(F^2) = \sum_{i=1}^{n} (F_o^2 - F_c^2) / \sum_{i=1}^{n} F_o^2, \ G = \sum_{i=1}^{n} (F_o^2 - F_c^2)^2 / (m-n)]^{1/2}.$$

Discussion

Molecular structure

The TAB molecule is shown in Fig. 1 viewed normal to the plane of the benzene ring. The interatomic distances and angles involving bonded atoms, and the nonbonded distances between neighbouring terminal



Fig. 1. Intramolecular distances (Å) and angles (°) with model viewed normal to the plane of the ring.

Table 4. Final fractional coordinates and anisotropic thermal parameters ($\times 10^4$)

The e.s.d.'s, which are enclosed in parentheses, correspond to the least significant digits in each case. The thermal parameters are defined for a temperature factor of the form exp $[-(b_{11}h^2 + b_{12}hk + b_{22}k^2 + b_{13}hl + b_{23}kl + b_{33}l^2)]$.

	r	ν	7	<i>b</i>	b.	<i>b</i> .	Ь	Ь	h
C(1)	22(2(2))	2700 (2)	2005 (2)	105 (4)		022	013	<i>U</i> ₂₃	<i>U</i> 33
C(1)	3303 (3)	3700 (2)	2905 (3)	105 (4)	12 (3)	22 (1)	61 (7)	0 (3)	205 (5)
C(2)	4891 (3)	3765 (2)	2274 (3)	107 (4)	22 (3)	25 (1)	59 (7)	5 (4)	204 (5)
C(3)	5617 (3)	4526 (2)	2131 (3)	88 (4)	16 (3)	26 (1)	63 (7)	4 (3)	166 (5)
C(4)	4818 (3)	5235 (2)	2618 (3)	88 (4)	8 (3)	25 (1)	28 (6)	-2(3)	150 (4)
C(5)	3288 (3)	5174 (2)	3244 (3)	85 (4)	7 (7)	23 (1)	46 (6)	0 (3)	155 (5)
C(6)	2563 (3)	4405 (2)	3378 (3)	98 (4)	8 (9)	23 (1)	46 (7)	0 (3)	185 (5)
C(11)	2641 (4)	2864 (2)	3028 (5)	127 (5)	9 (4)	23 (1)	126 (9)	2 (4)	316 (7)
C(31)	7266 (3)	4555 (2)	1458 (4)	98 (4)	25 (3)	32 (1)	89 (7)	3 (4)	182 (5)
C(51)	2386 (4)	5914 (2)	3784 (4)	93 (4)	7 (3)	24(1)	68 (7)	-14(3)	198 (5)
C(12)	918 (4)	2787 (2)	3401 (6)	134 (5)	-16(4)	31 (1)	151 (11)	-27(5)	416 (10)
C(32)	8160 (4)	5350 (2)	1530 (5)	119 (5)	-5(4)	40 (l)	122 (13)	-4(4)	251 (7)
C(52)	3008 (6)	6749 (2)	3412 (5)	135 (5)	8 (5)	23 (1)	89 (10)	-5(4)	309 (7)
O(1)	3435 (5)	2268 (2)	2793 (8)	192 (8)	17 (5)	24 (2)	393 (23)	2(8)	834 (24)
O(3)	7843 (5)	3941 (3)	878 (6)	153 (6)	33 (4)	40 (2)	181 (12)	-24(5)	301 (9)
O(5)	1156 (5)	5818 (2)	4516 (7)	140 (5)	-3(4)	33 (2)	232 (13)	-41(6)	414 (11)
H(2)	5523 (8)	3220 (4)	1909 (11)	180 (10)	35 (7)	34 (2)	133 (20)	-30(9)	363 (16)
H(4)	5364 (7)	5826 (3)	2508 (9)	143 (̈́9)	0(7)	33 (2)	107 (18)	2 (8)	306 (14)
H(6)	1391 (7)	4380 (3)	3868 (9)	144 (8)	5 (7)	33 (2)	126 (18)	-3(8)	318 (33)
H(11)	197 (10)	3109 (6)	2526 (21)	170 (12)	-2(13)	76 (4)	-30(35)	24(21)	652 (69)
H(12)	684 (11)	3074 (5)	4588 (14)	273 (15)	-64(13)	74 (4)	405 (33)	-52(16)	516(25)
H(13)	605 (10)	2151 (4)	3432 (19)	223 (13)	-32(9)	38 (3)	324 (38)	-23(15)	847 (43)
H(31)	8356 (15)	5558 (7)	2782 (15)	468 (26)-	- 261 (22)	102 (6)	231 (42)	-123(19)	401 (23)
H(32)	9240 (10)	5292 (6)	956 (17)	205 (13)	-40(12)	75 (12)	389 (36)	-67(18)	666 (35)
H(33)	7477 (10)	5815 (5)	847 (17)	249 (12)	-21(12)	60 (12)	46 (34)	175 (18)	708 (35)
H(51)	2240 (9)	7206 (4)	3 904 (14)	2 18 (8)	16 (16)	38 (8)	269 (28)	-42(11)	596 (25)
H(52)	4186 (9)	6824 (4)	3994 (16)	183 (9)	-51(9)	48 (9)	-27(29)	-3(14)	680 (32)
H(53)	3165 (16)	6830 (5)	2141 (14)	553 (14)	- 52 (14)	49 (14)	255 (41)	58 (12)	397 (22)

atoms, are indicated. It should be noted that corrections for thermal motion effects have not been applied. Those bond lengths and angles involving hydrogen which are not shown on Fig. 1 are given in Table 5.

Table 5. Bond distances and angles involving hydrogen The remaining hydrogen distances and angles are shown on Fig. 1

1.6.1.	
$C(12)-H(11) \\ C(12)-H(12) \\ C(11)-C(12)-H(11) \\ C(11)-C(12)-H(12) \\ H(11) \\ C(12)-H(12) \\ H(12) \\ C(12) \\ H(12) \\ H($	1.019 (11) Å 1.051 (11) 111.8 (6)° 112.3 (6) 101.5 (8)
H(11)-C(12)-H(12) H(11)-C(12)-H(13)	112.3 (8)
H(12)-C(12)-H(13)	110·7 (8)
C(32)-H(31) C(32)-H(33)	1·068 (10)
C(31)-C(32)-H(31)	112·0 (7)°
C(31)-C(32)-H(33) H(31)-C(32)-H(32)	10.3 (6)
H(31)-C(32)-H(33)	105.7 (9)
H(32)-C(32)-H(33)	108.3(8)
C(52) - H(52) C(52) - H(53)	1.004 (9) A 1.000 (11)
C(51)-C(52)-H(52)	110·5 (6)°
C(51)-C(52)-H(53) H(51)-C(52)-H(52)	112·0 (7) 109·7 (7)
H(51)-C(52)-H(53)	111.8 (8)
H(52)-C(52)-H(53)	102.4 (8)

The extent of pseudosymmetry associated with the molecule is of particular interest. The highest pointgroup symmetry possible for the molecule is 3m. While it can be said that the molecule approximates to this description, the disposition of the oxygen atoms and methyl groups breaks the threefold symmetry axis so that there are two pseudo-mirror planes normal to the plane of the ring and coincident with the bonds C(1)- C(4) and C(2)-C(5). This arrangement appears to have been adopted in order to minimize the number of intermolecular van der Waals contacts between methyl groups (see below).

Another feature of the molecule is the deviation of the oxygen and methyl carbon atoms from the central plane of the molecule as can be seen from the analysis of planarity summarized in Table 6. The non-hydrogen atoms of the acetyl group, together with the ring carbon to which the group is bonded, form a planar array inclined to the central plane of the molecule. Each group is therefore twisted about the $C(sp^2, ring)$ - $C(sp^2, acetyl)$ bond, giving the molecule a slight propeller-like appearance, similar to that observed in 1,3,5triphenylbenzene (Lonsdale, 1937), with torsion angles of 9.4, 8.2 and 8.9° for the groups bonded to C(1), C(3) and C(5), respectively. It is apparent that the rotation is due to intramolecular repulsive forces as the effect gives increased distances for contacts of the type $C(12)\cdots H(6)$ and $O(1)\cdots H(2)$. However a detailed analysis of these interactions is not feasible in view of the paucity of information in the literature on intramolecular van der Waals radii.

It is interesting to note that all three acetyl groups have a hydrogen atom residing within the group plane. The effect is probably due to either or both of the following interactions. First, there is the possibility of attraction between neighbouring oxygen and hydrogen atoms, and this is supported by the additional observation that each acetyl group bends slightly ($ca. 2^\circ$) towards the ring hydrogen atom situated adjacent to the oxygen. The second type of interaction to which the orientation of the methyl hydrogen atoms might be attributed is repulsion between the methyl and ring hydrogen atoms. This latter point is quite conceivable

Table 6. Least-squares planes for the central portion of the molecule and acetyl groups

The coefficients A, B, C, and D are defined such that Ax + By + Cz + D = 0. In the list of displacements from each plane the most significant figures of the positional standard deviations are enclosed in parentheses.

Coefficients	Displacements	Coefficients	Displacements
$ \begin{array}{rcl} A & 0.3462 \\ B & -0.0903 \\ C & 0.9338 \\ D & -2.447 \end{array} $	$\begin{array}{ccc} C(1) & 0.003 & (5) \text{ Å} \\ C(2) & -0.002 & (5) \\ C(3) & -0.003 & (5) \\ C(4) & -0.001 & (5) \\ C(5) & -0.001 & (5) \\ C(6) & -0.005 & (5) \\ C(11) & 0.002 & (6) \end{array}$	$ \begin{array}{rcl} A & 0.1999 \\ B & -0.0298 \\ C & 0.9794 \\ D & -2.528 \end{array} $	$\begin{array}{rrrr} C(1) & -0.002 \ (6) \ \text{\AA} \\ C(11) & 0.008 \ (6) \\ C(12) & -0.002 \ (6) \\ O(1) & -0.003 \ (8) \\ H(11) & -0.78 \ (2) \\ H(12) & 0.82 \ (2) \\ H(13) & -0.00 \ (2) \end{array}$
	$\begin{array}{cccc} C(31) & 0.003 & (5) \\ C(51) & 0.004 & (5) \\ H(2) & 0.01 & (1) \\ H(4) & -0.01 & (1) \\ H(6) & -0.00 & (1) \\ C(12) & -0.228 & (6) \\ O(1) & 0.157 & (8) \\ C(32) & 0.196 & (6) \\ C(32) & 0.142 & (9) \\ \end{array}$	$ \begin{array}{rcl} A & 0.3375 \\ B & -0.2317 \\ C & 0.9124 \\ D & -1.324 \end{array} $	$\begin{array}{cccc} C(3) & 0.000 & (5) \\ C(31) & -0.001 & (5) \\ C(32) & 0.000 & (6) \\ O(3) & 0.000 & (8) \\ H(31) & 0.82 & (2) \\ H(32) & -0.06 & (2) \\ H(33) & -0.83 & (2) \end{array}$
	$\begin{array}{ccc} O(3) & -0.142 & (8) \\ C(52) & -0.198 & (7) \\ O(5) & 0.170 & (7) \end{array}$	$ \begin{array}{rcl} A & 0.4645 \\ B & -0.0003 \\ C & 0.8856 \\ D & -3.396 \end{array} $	$\begin{array}{cccc} C(5) & 0.000 & (5) \\ C(51) & 0.001 & (5) \\ C(52) & 0.000 & (7) \\ O(5) & 0.000 & (7) \\ H(51) & 0.02 & (2) \\ H(52) & 0.84 & (2) \\ H(53) & -0.77 & (2) \end{array}$

in view of similar effects observed in various overcrowded molecules.

The bonded interatomic distances and associated angles agree satisfactorily with values given in the literature for covalent bonds in similar environments to those found in TAB. It is unfortunate that there is very little available in the literature describing the geometry of the acetyl group. A pleasing feature of the results is the agreement between the chemically-equivalent distances (see Table 7), thus confirming the reliability of the error estimates quoted for the positional parameters.

Table 7. Bond distances (in Å) for the final least-squares positions, uncorrected for librational effects

The e.s.d.'s (enclosed in parentheses) are quoted for the least significant digits.

		Mean
C(1)-C(2) C(2)-C(3) C(3)-C(4) C(4)-C(5) C(5)-C(6) C(6)-C(1)	1·402 (4) 1·390 (3) 1·400 (3) 1·401 (3) 1·402 (3) 1·392 (3)	1.398 (2)
C(1)-C(11) C(3)-C(31) C(5)-C(51)	1·499 (3) 1·507 (3) 1·497 (3)	1.501 (2)
C(11)-C(12) C(31)-C(32) C(51)-C(52)	1·496 (4) 1·498 (4) 1·495 (3)	1·496 (2)
C(11)-O(1) C(31)-O(3) C(51)-O(5)	1·200 (5) 1·210 (4) 1·215 (5)	1.208 (3)
C(2)-H(2) C(4)-H(4) C(6)-H(6)	1·083 (6) 1·074 (5) 1·075 (6)	1.077 (3)
C(12)-H(11) C(12)-H(12) C(12)-H(13) C(32)-H(31) C(32)-H(32) C(32)-H(32) C(32)-H(33) C(52)-H(51) C(52)-H(52) C(52)-H(53)	$\begin{array}{c} 1.019 \ (11) \\ 1.051 \ (11) \\ 1.071 \ (7) \\ 1.019 \ (11) \\ 1.035 \ (9) \\ 1.068 \ (10) \\ 1.069 \ (8) \\ 1.064 \ (9) \\ 1.000 \ (11) \end{array}$	1.044 (3)

Molecular packing

The crystal structure is shown in Fig. 2 in a view down c*. The molecules are bonded into layers separated by approximately c/4. Within the layers the molecules are linked by van der Waals attraction through contacts of the type $O \cdots CH_3$ and $CH_3 \cdots CH_3$. The predominance of the former type facilitates higher packing efficiency.

A complete list of intermolecular distances is given in Table 8. Contacts have been included if the appropriate distance does not exceed the sum of the van der Waals radii (Pauling, 1960) by more than 0.2 Å. Note that for $0 \cdots H$ -C contacts the data are tabulated if either $0 \cdots H$ or $0 \cdots C$ satisfies the criterion. A similar procedure has been adopted in accepting C-H \cdots H-C contacts according to either the H \cdots H or C \cdots C distances. A feature of interest is that the acetyl groups bonded to C(1) and C(5) form most of the close contacts. This may well explain why the group bonded to C(3) has the least pronounced thermal motion of the three groups.

Table 8. Intermolecular close contacts (Å)

The criteria used to accept contacts for inclusion in the table are given in the text.

O····C contacts	$\mathbf{O}\cdots\mathbf{H}$	$0\!\cdots\!C$
$\int H(4^{iv}) - C(4^{iv})$	2.58	3.65
$O(1) \cdots \{ H(33^{iv}) - C(32^{iv}) \}$	2.72	3.46
$H(52^{iv})-C(52^{iv})$	2.59	3.29
$O(3) \cdots H(11^v) - C(12^v)$	2.65	3.64
$\int H(31^{11}) - C(32^{11})$	2.65	3.37
$O(5) \cdots \{ H(6^{11'}) - C(6^{11'}) \}$	2.56	3.62
$H(12^{11''})-C(12^{11''})$	2.50	3.33
$\mathbf{C} \cdots \mathbf{C}$ contacts	$C \cdots C$	н∙∙∙н
$C(2)-H(2)\cdots H(52^{iv})-C(52^{iv})$	3.79	2.40
$C(32^{ii})-H(32^{ii})\cdots H(32^{i'})-C(32^{i'})$	4.19	2.22
$C(12)-H(11)\cdots H(51^{111})-C(52^{111})$	3.88	2.69
$C(3) \cdots C(51^{i''})$	3.52	-
$C(4) \cdots C(5^{i''})$	3.51	-
$C(4) \cdots C(31^{i'})$	3.49	-

Rigid-body motion

The procedure adopted in analysing the rigid-body motion of the molecule was the TLX method proposed



Fig. 2. Packing diagram as viewed down c*. The equivalent position symbols are defined in Table 8.

Table 8 (cont.)

Equivalent position notation Without superscript $(x, y, z)^*$ i' (1-x, 1-y, -z) i'' (1-x, 1-y, 1-z)ii (-1+x, y, z) ii' (-x, 1-y, -z) ii'' (-x, 1-y, 1-z)iii $(-x, -\frac{1}{2}+y, \frac{1}{2}-z)$ iv $(1-x, -\frac{1}{2}+y, \frac{1}{2}+z)$ * Position i in Fig. 2.

by Pawley (1963, 1970) which uses iterative leastsquares calculations to fit the translational and librational tensors T and L, and the origin of L, to the final set of atomic U tensors. The calculation was first performed for all atoms in the molecule. As might be expected this gave extremely poor agreement between the calculated and observed U tensors, due no doubt to the complexity of the modes associated with the acetyl groups. A subsequent analysis involving only the nine central carbon atoms and the ring hydrogen atoms improved the level of agreement, although the hydrogens did show excess motion which can be attributed to stretching and bending modes. The final calculations, for which the results are reported in Tables 9-11, were therefore conducted with zero weights assigned to the ring hydrogens. Agreement between the calculated and observed U tensors is satisfactory for the nine central carbons. The preferred rigid-body vibration is normal to the plane of the molecule and the preferred libration axis lies close to molecular axis 1.

Table 9. Rigid-body T and L elements referred to the molecular axes

Axis 1 is directed along the direction C(6)-C(3); axis 2 is along the direction C(1)-C(5); axis 3 is perpendicular to the molecular plane.

$\mathbf{L} = \begin{bmatrix} 14.8 & & \\ -0.7 & 3.0 & \\ 1.0 & -0.7 & 3.0 \end{bmatrix} (deg^2)$	

Origin of L axes in the molecular axial system, -0.28, 0.38, -0.13 Å.

Table 10. R.m.s. values for the principal axes of the T and L tensors referred to the system of molecular axes

Tensor	R.m.s. value	Direction cosines relative to molecular axes			
		Axis 1	Axis 2	Axis 3	
	0∙22 Å	-0.076	0.169	0.983	
Т	0.19	0.712	0.700	-0.065	
	0.16	0.698	-0.694	0.174	
	3·8°	0.995	-0.023	0.088	
L	1.9	-0.101	0.669	0.736	
	1.5	-0.050	0 ·741	0.671	

A more detailed analysis of the thermal motion is being conducted in this laboratory.

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Table 11. The observed and calculated vibration components ($Å^2 \times 10^3$) referred to the molecular axial system

	U_{11}		U	U_{12}		U_{22}		U13		U_{23}		U_{33}	
	obs	cal	obs	cal	obs	cal	obs	cal	obs	cal	obs	cal	
C(1)	36	33	3	3	30	31	-3	-3	4	4	61	57	
C(2)	37	33	6	5	34	32	-3	-2	7	4	60	57	
C(3)	29	31	4	4	35	34	-1	-1	4	3	51	49	
C(4)	32	31	3	3	34	32	-3	-2	1	3	44	50	
C(5)	29	31	2	4	31	31	-2	-2	2	2	46	49	
C(6)	34	31	2	3	31	32	-4	-2	3	4	54	48	
C(11)	40	39	2	1	31	32	- 5	- 5	8	6	96	86	
C(31)	30	31	9	5	43	40	1	-2	5	5	57	55	
C(51)	31	35	4	6	31	33	-4	-3	0	1	60	66	
H(2)	60	37	14	7	44	33	-5	-3	2	4	111	75	
H(4)	47	34	-1	1	45	33	-4	-4	5	3	92	63	
H(6)	45	31	2	3	45	36	-4	-2	5	4	97	51	