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A Refinement of the Crystal and Molecular Structure of Hydrazinium Sulphate by Neutron Diffraction

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The structure of hydrazinium sulphate, $N_2H_6SO_4$, has been redetermined by neutron diffraction. This structural determination has been compared, by means of half-normal probability plot analysis and χ^2 tests, with existing neutron and X-ray structure determinations. Identical molecular geometries have been obtained in all three determinations.

Introduction

Considerable interest has been shown by a number of workers in the structural details of a number of salts of hydrazine (Kvick, Jönsson & Liminga, 1972; Liminga & Lundgren, 1965; Nitta, Sakurai & Tomiee, 1951; Anderson, Vilminot & Brown, 1973). Since these compounds have complex hydrogen-bonding schemes, many of which are imperfectly understood, they are eminently suitable for detailed examination by neutron diffraction.

Hydrazinium sulphate was chosen for investigation as it was readily available and easily produced crystals large enough for neutron diffraction. The work reported here was at an advanced stage when a previously overlooked paper by Jönsson & Hamilton (1970) was brought to our attention. Their paper reports the results of a very accurate X-ray and a somewhat lower-accuracy neutron structure determination of hydrazinium sulphate.

Jönsson & Hamilton's neutron data set was badly affected by secondary extinction and was somewhat restricted. The present data set was somewhat more extensive and was also less severely affected by secondary extinction, although the crystal had not been specially treated in any way. Accordingly refinement was completed and the data sets objectively compared using half-normal probability plots and χ^2 tests.

Experimental

A single crystal of about 15 mm^3 volume, grown from the slow evaporation of an aqueous solution, was mounted with the *c* crystallographic axis approximately parallel to the φ axis of the Australian Institute of Nuclear Science and Engineering's computer-controlled four-circle diffractometer 2TanA. Four sets of equivalent reflexions, totalling 3600 observations, were collected by the ω–2θ scan technique for $2\theta \leq 100°$. A standard reflexion, monitored every 25 observations, showed no systematic variation during the course of data collection. The data were corrected for absorption and Lorentz effects and averaged to yield a set of 899 unique reflexions, all of which were included in the least-squares refinement. The neutron wavelength was 0·981 Å. Cell parameters were redetermined using several hundred centred reflexions measured on the diffractometer.

Crystal data

Hydrazinium sulphate; $N_2H_6SO_4$; orthorhombic; space group $P2_12_12_1$ (No. 19); $a=8{\cdot}232(5)$, $b=9{\cdot}145(5)$, $c=5{\cdot}535(2)$ Å; $Z=4$; calculated linear absorption coefficient for neutrons $=1{\cdot}99\pm0{\cdot}05$ cm^{-1} (using a value of 36 barns for the incoherent absorption cross-section of hydrogen).

Structure solution and refinement

The heavy-atom parameters of Nitta, Sakurai & Tomiie (1951) were used as input into a single structure-factor calculation followed by a Fourier map. All hydrogen-atom positions were clearly visible and unambiguous positional parameters were assigned. Refinement was carried out using the Brookhaven full-matrix least-squares program *LINUS*. Anisotropic thermal parameters for all atoms, together with an isotropic extinction parameter, were allowed to vary in the final least-squares cycles. Parameter shifts in the final cycles were negligible.

The function minimized was $\sum w(|F_o^2|-|F_c^2|)^2$ where w, the weight of an individual reflexion was defined as $w^{-1}=\sigma^2(F_o^2)$. The variances of individual reflexions were assigned on the basis of a least-squares polynomial regression of the form $\sigma_m^2(I)=\sum_{n=1}^{N} A_nI^{n-1}$ to determine A_n, where $\sigma_m^2(I)$ is the variance of the mean obtained from each group of equivalent reflexions. The analysis was performed on the absorption corrected intensities before the application of the Lorentz correction. This approach was adopted in order to estimate non-counting errors in the data set. Individual variances estimated from the polynomial were constrained to be at least equal to the variance estimated from Poisson counting statistics. This was necessary to guard against the case of the polynomial of best fit underestimating $\sigma^2_m(I)$ for certain portions of the data in order to estimate better the remainder. In practice very few reflexions fell into this category. Final agreement factors are shown in Table 1.* The neutron scattering lengths used, in units of 10^{-12} cm, were N = 0·940, O = 0·577, S = 0·280 and H = −0·372.

Table 1. *Final agreement factors for hydrazinium sulphate*

$$R(F_o^2)=\sum||F_o^2|-|F_c^2||/\sum|F_o^2|=0{\cdot}060$$
$$R_w(F_o^2)=[\sum w(|F_o^2|-|F_c^2|)^2/\sum w|F_o^4|]^{1/2}=0{\cdot}076$$
$$R(F_o)=\sum||F_o|-|F_c||/\sum|F_o|=0{\cdot}049$$
$$S=[\sum w(|F_o^2|-|F_c^2|)^2/(m-n)]^{1/2}=1{\cdot}61 \text{ for } (m-n)=780$$

where

m = number of observations in the refinement,
n = number of parameters varied in the refinement.

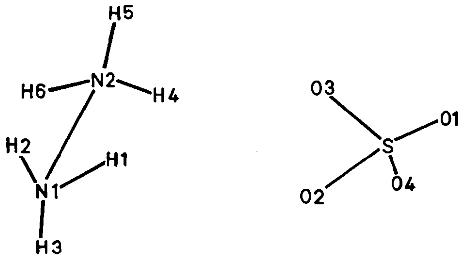

Fig. 1. Numbering scheme for hydrazinium sulphate.

The value of 0·917(9) × 10^{-12} cm for the neutron scattering length of nitrogen (Kvick, Koetzle, Thomas & Takusagawa, 1974) has recently been reported. This value, however, was reported too late for inclusion in this structure determination. Accordingly the nitrogen thermal parameters reported here will be slightly too high.

Discussion

The positional and thermal parameters obtained at the completion of refinement are shown in Table 2. Bond

Table 3. *Bond lengths* (Å) *and angles* (°) *for hydrazinium sulphate*

	This investigation	Jönsson & Hamilton (1970)	
		Neutron	X-ray
S——O(1)	1·482 (3)	1·498 (5)	1·491 (1)
S——O(2)	1·478 (4)	1·475 (5)	1·483 (1)
S——O(3)	1·465 (4)	1·465 (5)	1·468 (1)
S——O(4)	1·467 (4)	1·463 (5)	1·468 (1)
N(1)–N(2)	1·416 (2)	1·426 (3)	1·418 (2)
N(1)–H(1)	1·048 (4)	1·036 (6)	0·76 (2)
N(1)–H(2)	1·061 (4)	1·059 (5)	0·85 (2)
N(1)–H(3)	1·050 (4)	1·039 (5)	0·81 (2)
N(2)–H(4)	0·972 (6)	0·989 (7)	0·74 (3)
N(2)–H(5)	0·981 (7)	0·989 (11)	0·80 (4)
N(2)–H(6)	0·965 (7)	0·952 (13)	1·02 (4)
O(1)–S——O(2)	108·7 (0·2)	107·9 (0·4)	108·3 (0·1)
O(1)–S——O(3)	109·2 (0·2)	108·8 (0·3)	109·0 (0·1)
O(1)–S——O(4)	109·0 (0·2)	108·6 (0·3)	108·7 (0·1)
O(2)–S——O(3)	108·7 (0·2)	108·9 (0·3)	108·9 (0·1)
O(2)–S——O(4)	109·8 (0·2)	110·2 (0·3)	109·9 (0·1)
O(3)–S——O(4)	111·5 (0·2)	112·2 (0·4)	112·0 (0·1)
N(2)–N(1)–H(1)	108·0 (0·3)	107·5 (0·4)	110·7 (1·9)
N(2)–N(1)–H(2)	108·3 (0·2)	107·8 (0·4)	109·0 (1·5)
N(2)–N(1)–H(3)	109·3 (0·3)	109·3 (0·4)	110·5 (1·8)
N(1)–N(2)–H(4)	111·6 (0·4)	110·0 (0·6)	110·6 (2·8)
N(1)–N(2)–H(5)	109·2 (0·4)	108·4 (0·6)	108·6 (2·2)
N(1)–N(2)–H(6)	112·6 (0·4)	109·5 (0·8)	103·6 (1·7)
H(1)–N(1)–H(2)	109·0 (0·3)	110·3 (0·5)	108·1 (2·1)
H(1)–N(1)–H(3)	111·5 (0·4)	111·0 (0·5)	102·0 (2·3)
H(2)–N(1)–H(3)	110·6 (0·4)	110·8 (0·5)	116·3 (1·8)
H(4)–N(2)–H(5)	106·7 (0·7)	107·3 (1·1)	114·3 (3·5)
H(4)–N(2)–H(6)	112·4 (0·8)	113·9 (1·3)	108·6 (3·9)
H(5)–N(2)–H(6)	103·9 (0·8)	107·6 (1·4)	110·7 (4·1)

Table 2. *Final positional and thermal parameters for hydrazinium sulphate*

The positional parameters are given as fractional coordinates × 10^4. The anisotropic thermal parameters (× 10^4) are defined as $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$.

The isotropic extinction parameter g = 0·22 (2).
The notation of Coppens & Hamilton (1970) is used.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S	−497 (3)	692 (3)	2123 (4)	44 (3)	35 (2)	92 (6)	−2 (2)	5 (4)	5 (4)
O(1)	792 (2)	862 (2)	277 (3)	55 (1)	48 (1)	120 (4)	−4 (1)	23 (2)	4 (2)
O(2)	262 (2)	719 (2)	4543 (2)	98 (2)	59 (1)	105 (4)	−12 (2)	−24 (2)	3 (2)
O(3)	−1632 (2)	1920 (2)	1938 (3)	60 (1)	59 (1)	229 (5)	17 (1)	15 (3)	13 (2)
O(4)	−1322 (2)	−712 (2)	1746 (3)	78 (2)	52 (1)	144 (4)	−24 (1)	13 (2)	−12 (2)
N(1)	91 (1)	3340 (1)	7663 (2)	56 (1)	50 (1)	125 (2)	1 (1)	−6 (1)	2 (1)
N(2)	−1535 (1)	3125 (1)	6906 (2)	56 (1)	74 (1)	173 (3)	−1 (1)	7 (1)	−20 (1)
H(1)	789 (3)	3586 (4)	6134 (6)	83 (3)	111 (4)	276 (11)	−19 (3)	50 (5)	−14 (5)
H(2)	119 (4)	4244 (3)	8864 (5)	126 (4)	87 (3)	201 (7)	−15 (3)	−21 (5)	−27 (4)
H(3)	510 (4)	2390 (4)	8528 (7)	123 (4)	94 (3)	282 (11)	34 (3)	−40 (6)	32 (5)
H(4)	−1619 (6)	2340 (6)	5729 (13)	166 (7)	196 (7)	892 (36)	−4 (6)	−144 (14)	−278 (14)
H(5)	−1927 (7)	4014 (6)	6107 (12)	219 (9)	186 (7)	722 (29)	84 (7)	−239 (14)	−45 (13)
H(6)	−2271 (6)	2996 (11)	8245 (12)	125 (6)	627 (24)	458 (22)	−173 (11)	47 (11)	36 (21)

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31054 (11 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

lengths and angles are shown in Table 3 while the hydrogen bonding scheme is summarized in Table 4. Estimated standard deviations have been derived from the full variance-covariance matrix of the least-squares refinement. The results of Jönsson & Hamilton (1970) are included for comparison. The labelling of the atoms is that of Jönsson & Hamilton (1970) and is shown in Fig. 1.

The gross features of the structure are in close agreement with those found by Jönsson & Hamilton (1970). Some small improvement in the accuracy of the bond lengths and angles has been achieved. The staggered conformation of the $N_2H_6^{2+}$ ion has been confirmed, as have been the large thermal parameters of the hydrogen atoms bonded to N(2). No attempt to correct these bond lengths for thermal motion has been attempted since, as Jönsson & Hamilton (1970) have pointed out, no satisfactory model for such corrections exists.

An attempt to collect neutron data at liquid nitrogen temperatures in order to reduce the thermal motion of the atoms failed since the crystals used shattered as the temperature was lowered. To investigate whether the shattering was caused by thermal shock or by some other means, such as a phase transition, neutron powder patterns were run at both ambient and liquid nitrogen temperatures. The powder patterns suggest that a phase transition may be occurring, although few peaks are discernible above the high background arising from incoherent scattering by the hydrogen atoms. No transition temperature has been recorded.

An inspection of Tables 3 and 4 indicates that the agreement between the three structure determinations, except, as is expected, for X-ray hydrogen atom parameters, is satisfactory. To examine the agreement more closely the following half-normal probability plots (Abrahams & Keve, 1971) were constructed. (*a*) Neutron thermal parameters. (*b*) Neutron positional parameters. (*c*) Our neutron and the X-ray heavy-atom positional parameters. (*d*) Jönsson & Hamilton's (1970) neutron and X-ray heavy-atom positional parameters. The exact values of the half-normal order statistics for small samples (Hamilton & Abrahams, 1972) were used for all plots except (*a*), for which the population is sufficiently large to allow the use of the percentage points of the normal distribution. These plots are shown in Fig. 2. In addition, further comparisons of individual parameters were made using χ^2 tests. The values of R^2 which may be tested as χ^2 (Hamilton, 1969) are listed in Table 5.

Examination of the plot and χ^2 test for each individual case revealed:

(*a*) That it is improbable that the neutron thermal parameters derived from the two independent data

Table 4. *Hydrogen bonds and short van der Waals contacts in hydrazinium sulphate*

The values of Jönsson & Hamilton (1970) are given as the second line of each entry. The notation is that of Jönsson & Hamilton (1970), who have previously discussed the classification of these contacts into hydrogen bonds and short van der Waals contacts.

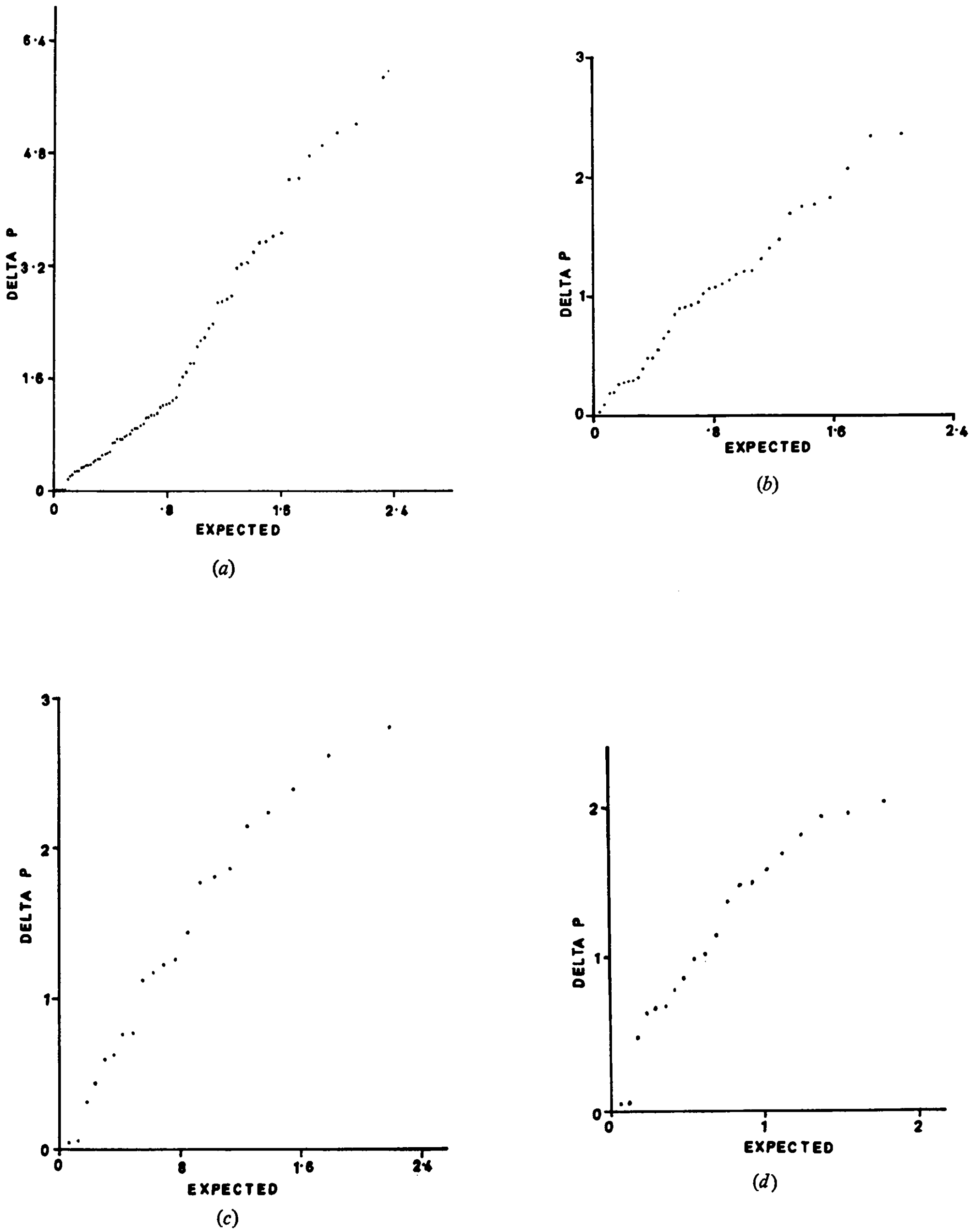
N	H	O	N···O	N–H	H···O	∠N–H···O	∠H···O–S
N(1)	H(1)	O(4)	2·781 (2) Å	1·048 (4) Å	1·774 (5) Å	160·0 (0·4)°	109·3 (0·2)°
			2·782 (3)	1·036 (6)	1·784 (7)	160·4 (0·6)	109·8 (0·3)
N(1)	H(1)	O(3)	2·717 (2)	1·048 (4)	2·421 (5)	94·8 (0·3)	112·4 (0·2)
			2·721 (4)	1·036 (6)	2·434 (7)	94·6 (0·4)	112·0 (0·3)
N(1)	H(1)	O(1)	2·915 (2)	1·048 (4)	2·576 (5)	98·2 (0·3)	76·2 (0·2)
			2·921 (3)	1·036 (6)	2·586 (7)	98·3 (0·4)	76·3 (0·2)
N(1)	H(2)	O(2)	2·685 (2)	1·061 (4)	1·642 (4)	166·5 (0·4)	113·1 (0·2)
			2·689 (3)	1·059 (5)	1·646 (6)	167·0 (0·5)	112·7 (0·3)
N(1)	H(2)	O(4)	3·369 (3)	1·061 (4)	2·624 (4)	126·9 (0·3)	73·0 (0·2)
			3·369 (3)	1·059 (5)	2·622 (6)	127·2 (0·4)	72·9 (0·2)
N(1)	H(3)	O(1)	2·749 (2)	1·050 (4)	1·715 (5)	167·3 (0·4)	112·2 (0·2)
			2·752 (3)	1·039 (5)	1·730 (6)	166·9 (0·6)	112·0 (0·3)
N(1)	H(3)	O(3)	2·717 (2)	1·050 (4)	2·450 (5)	93·1 (0·3)	144·8 (0·2)
			2·721 (4)	1·039 (5)	2·449 (8)	93·7 (0·4)	144·0 (0·3)
N(1)	H(3)	O(3)	3·049 (3)	1·050 (4)	2·618 (5)	104·1 (0·3)	75·3 (0·2)
			3·045 (4)	1·039 (5)	2·627 (8)	103·7 (0·4)	76·0 (0·2)
N(2)	H(4)	O(3)	2·963 (3)	0·972 (6)	2·133 (9)	142·4 (0·8)	93·8 (0·3)
			2·961 (4)	0·989 (7)	2·115 (14)	142·5 (1·2)	92·9 (0·4)
N(2)	H(4)	O(2)	2·956 (3)	0·972 (6)	2·242 (7)	129·5 (0·5)	89·1 (0·2)
			2·955 (4)	0·989 (7)	2·212 (9)	130·9 (0·8)	88·8 (0·4)
N(2)	H(4)	O(4)	2·826 (2)	0·972 (6)	2·325 (8)	111·2 (0·7)	158·8 (0·2)
			2·830 (3)	0·989 (7)	2·344 (12)	109·4 (1·0)	158·0 (0·3)
N(2)	H(5)	O(1)	2·846 (2)	0·981 (7)	2·078 (9)	133·9 (0·6)	119·4 (0·3)
			2·850 (3)	0·989 (11)	2·064 (13)	134·9 (0·8)	119·4 (0·4)
N(2)	H(5)	O(2)	2·952 (3)	0·981 (7)	2·354 (7)	118·6 (0·6)	106·2 (0·3)
			2·960 (4)	0·989 (11)	2·373 (10)	117·3 (0·9)	106·8 (0·4)
N(2)	H(6)	O(1)	2·851 (2)	0·965 (7)	2·074 (10)	136·4 (1·0)	109·4 (0·3)
			2·851 (3)	0·952 (13)	2·119 (16)	132·6 (1·6)	110·8 (0·5)
N(2)	H(6)	O(3)	2·996 (3)	0·965 (7)	2·329 (10)	125·7 (0·7)	122·0 (0·3)
			2·991 (4)	0·952 (13)	2·285 (17)	130·4 (1·2)	121·4 (0·5)
N(2)	H(6)	O(4)	2·826 (2)	0·965 (7)	2·529 (10)	97·8 (0·7)	152·6 (0·3)
			2·830 (3)	0·952 (13)	2·544 (17)	97·5 (1·2)	151·9 (0·4)

sets belong to the same population. The half normal probability plot is markedly non-linear and only $R^2\beta_{11}$ lies within the 95% probability levels of χ^2.

(*b*) No detectable difference in magnitude between the two sets of neutron positional parameters. However, the χ^2 values may indicate that the agreement between the y and z parameters is perhaps better than would be expected for a normal distribution.

(*c*) and (*d*) That the neutron and X-ray positional parameters probably belong to the same population.

From the findings presented above it may be concluded with some confidence that, with the exception of the X-ray hydrogen atom positions, the three structural determinations of hydrazinium sulphate lead to identical molecular geometries. The systematic differences between X-ray and neutron positional pa-



(*a*) (*b*) (*c*) (*d*)

Fig. 2. Half-normal probability plots for hydrazinium sulphate (see text for explanation).

Table 5. χ^2 *tests for hydrazinium sulphate derived parameters*

(*a*) Neutron thermal parameters

$R^2_{\beta 11} = 68\cdot5$ $\quad R^2_{\beta 13} = 12\cdot5$
$R^2_{\beta 22} = 155\cdot5$ $\quad R^2_{\beta 23} = 19\cdot8$
$R^2_{\beta 33} = 136\cdot3$ $\quad \chi^2_{2.5,80} = 106\cdot6$
$R^2_{\beta 12} = 8\cdot65$ $\quad \chi^2_{97.5,80} = 57\cdot15$

(*b*) Neutron positional parameters

$R^2_x = 43\cdot7$ $\quad \chi^2_{2.5,40} = 59\cdot34$
$R^2_y = 16\cdot5$ $\quad \chi^2_{97.5,40} = 24\cdot43$
$R^2_z = 8\cdot8$

(*c*) Neutron (this investigation) X-ray positional parameters

$R^2_x = 15\cdot2$ $\quad \chi^2_{2.5,21} = 35\cdot48$
$R^2_y = 15\cdot0$ $\quad \chi^2_{97.5,21} = 10\cdot28$
$R^2_z = 19\cdot5$

(*d*) Neutron X-ray positional parameters (Jönsson & Hamilton)

$R^2_x = 19\cdot0$ $\quad \chi^2_{2.5,21} = 35\cdot48$
$R^2_y = 10\cdot6$ $\quad \chi^2_{97.5,21} = 10\cdot28$
$R^2_z = 8\cdot0$

rameters are well known and will not be commented on further here. The differences between the neutron thermal parameters are probably due to the dissimilar extinction behaviours exhibited by the two crystals, since the form of the extinction function correlates very strongly with the thermal parameters.

In conclusion it may be noted that the two neutron diffraction investigations have produced identical descriptions of the molecular geometries of hydrazinium sulphate, although carried out at different reactors using different samples. The less severe extinction effects in the present investigation have probably led to somewhat improved thermal parameters.

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The Crystal Structure of 1,2,3,4-Tetrachloro-9-t-butyltriptycene

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1,2,3,4-Tetrachloro-9-t-butyltriptycene forms monoclinic crystals with the space group $P2_1/c$, lattice constants $a = 10\cdot231$ (1), $b = 18\cdot865$ (2), $c = 10\cdot631$ (1) Å, $\beta = 99\cdot60$ (1)° and $Z = 4$. The structure was solved by conventional Patterson and Fourier techniques and refined by the block-diagonal least-squares method to an *R* value of 0·049 for the 3038 observed reflexions collected by diffractometry. On account of the bulky t-butyl and chlorine substituents in the *peri* position, the molecule is overcrowded and C(9)–C(17) and C(9)–C(21) are 1·603 and 1·576 Å long and, as expected, contribute to the relaxation. Also, the t-butyl and *peri* chlorine substituents are inclined in opposite directions. Some of the shortest intramolecular distances between chlorine and hydrogen atoms are 2·604, 2·685 and 2·590 Å.

Introduction

Triptycene is known to have a rigid molecular structure. In the case of its 9-substituted derivatives, the internal rotation around C(9)–C(21) is restricted by the steric effect, and some rotational isomers were confirmed by a proton magnetic resonance study (Suzuki, Ōki & Nakanishi, 1974). 1,2,3,4-Tetrachloro-9-t-butyltriptycene has an overcrowded molecular structure, and considerable distortion is expected owing to the bulky substituents. Crystals of this compound have been subjected to X-ray crystal analysis in