to be the same as those observed but making all C—H bond lengths 1·10 Å. The effect of this calculation on the non-bonded contacts listed in Table 3 is indicated by the entries in the column headed 'With ideal C—H distances'.

Thus the crystal structure shows the features predicted by the potential-energy calculations. The HMB C atoms are not coplanar, although they are more so than the minimum-energy structure for an isolated molecule. The flatness of the minimum with respect to planarity facilitates a shorter TCNE–HMB interplanar spacing. The TCNE molecules in the two alternative positions have very similar non-bonded interactions with the HMB.

References

Allen, P. S. & Cowking, A. (1967). *J. Chem. Phys.* **47**, 4286–4289.

Boyd, R. H. (1968). *J. Chem. Phys.* **49**, 2574–2583.

Boyd, R. H., Breitling, S. M. & Mansfield, M. (1973). *Am. Inst. Chem. Eng. J.* **19**, 1016–1024.

Coulson, C. A. (1970). *Thermal Neutron Diffraction*, edited by B. T. M. Willis, pp. 72–73. Oxford Univ. Press.

Coulson, C. A. & Stocker, D. (1959). *Mol. Phys.* **2**, 397–406.

Cruickshank, D. W. J. (1956). *Acta Cryst.* **9**, 754–756; 757–758.

Hamilton, W. C. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 288–292. Birmingham: Kynoch Press.

Hamilton, W. C., Edmonds, J. W., Tippe, A. & Rush, J. J. (1969). *Discuss. Faraday Soc.* **48**, 192–204.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 73, 102. Birmingham: Kynoch Press.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

Karl, R. R. Jr, Wang, Y. C. & Bauer, S. H. (1975). *J. Mol. Struct.* **25**, 17–34.

Maverick, E., Smith, S., Kozerski, L., Anet, F. A. L. & Trueblood, K. N. (1975). *Acta Cryst.* B**31**, 805–815.

Mighell, A. D., Santoro, A. & Donnay, J. D. H. (1969). *International Tables for X-ray Crystallography*, Vol. I, 3rd ed., pp. 530–535. Birmingham: Kynoch Press.

Overberger, J. E., Steele, W. A. & Aston, J. G. (1969). *J. Chem. Thermodyn.* **1**, 535–542.

Ron, A. & Hyams, I. J. (1972). *Chem. Phys. Lett.* **17**, 557–560.

Saheki, M., Yamada, H., Yoshioka, H. & Nakatsu, K. (1976). *Acta Cryst.* B**32**, 662–664.

Santoro, A. & Mighell, A. D. (1970). *Acta Cryst.* A**26**, 124–127.

Strouse, C. E. (1970). *Acta Cryst.* A**26**, 604–608.

Strouse, C. E. (1976). *Rev. Sci. Instrum.* **47**, 871–876.

Ware, B., Williamson, K. & Devlin, J. P. (1968). *J. Phys. Chem.* **72**, 3970–3974.

Williams, D. E. (1969). *Acta Cryst.* A**25**, 464–470.

Acta Cryst. (1978). B**34**, 2781–2785

The Crystal Structure of Guanidinium Pyromellitate Trihydrate Monoperhydrate

By J. M. Adams and Vijayalakshmi Ramdas

Edward Davies Chemical Laboratories, University College of Wales, Aberystwyth SY23 1N3, Wales

(*Received* 16 *March* 1978; *accepted* 21 *April* 1978)

The structure of $[C(NH_2)_3]_4(O_2C)_2C_6H_2(CO_2)_2.3H_2O.H_2O_2$ has been solved using microdensitometer-measured data and refined to $R = 0{\cdot}096$. The space group is $P\bar{1}$ [$a = 7{\cdot}35$ (2), $b = 10{\cdot}03$ (2), $c = 10{\cdot}24$ (2) Å, $\alpha = 105{\cdot}5$ (3), $\beta = 116{\cdot}4$ (2), $\gamma = 72{\cdot}3$ (2)°] and the H_2O_2 molecules substitute in two equivalent water molecule positions with site occupancy of approximately one-half. All of the H atoms of the guanidinium ions are involved in the hydrogen-bonding scheme. The hydrogen peroxide molecules accept three hydrogen bonds and donate two. The carboxyl groups of the pyromellitate fragment are twisted by 15·9 and 84·5° with respect to the benzene ring, values significantly different from those found in pyromellitic acid dihydrate (21·4 and 74·5°).

Introduction

The title compound is of interest since it is one of a relatively small number of compounds containing hydrogen peroxide of crystallization (perhydrates) which are reasonably stable. It is also only the second salt hydrate perhydrate to be studied structurally, the first being guanidinium oxalate dihydrate monoperhydrate (Adams & Pritchard, 1976). Perhydrates have many technological uses and some basic structural work is necessary to lay a foundation for 'chemical engineering' of stable, industrially useful peroxide carriers (Adams, Pritchard & Thomas, 1976).

Experimental

12·7 g of pyromellitic acid (1,2,4,5-benzenetetracarboxylic acid) and 18 g of guanidinium carbonate were dissolved in hot water and upon crystallization guanidinium pyromellitate tetrahydrate crystals were formed. Recrystallization from 30% (w/v) hydrogen peroxide solution gave colourless parallelepipeds which turned white on exposure to air. A thermogravimetric analysis (TGA) of the hydrate and perhydrate showed that the weight loss of the hydrate occurred in one smooth step (corresponding to $4H_2O$) whereas for the perhydrate the loss could be clearly seen to take place in two stages (Fig. 1). Since it is known that H_2O_2 is usually lost from solids at temperatures greater than those for H_2O loss from related structures, the TGA was interpreted as evidence of a salt.$3H_2O.H_2O_2$. The presence of H_2O_2 in the crystals was proven by tests with acidified Ti^{IV} and determined iodometrically. This perhydrate is not stable at room temperature: it decomposes continuously with small explosions.

Oscillation and Weissenberg photographs showed that the crystals were triclinic. Cell parameters (Table 1) were obtained by a least-squares refinement from high-angle Weissenberg data. Two data sets were collected from different batches of crystals: (i) 0–4*kl* and *hk*0 which gave 1082 unique reflections and (ii) *h*0*l*–*h*6*l* and *hk*1–*hk*6 which gave 1153 unique reflections, or 1427 when merged with the first data set. The films were processed by the SRC Microdensitometer Service. Interlayer scale factors within each data set were obtained using the cross levels; the data sets were merged using a least-squares fit on common reflections. These scale factors were refined.

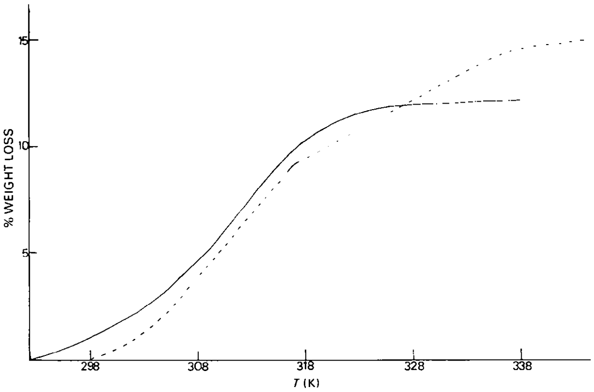

Fig. 1. Thermogravimetric analytical curve for guanidinium pyromellitate tetrahydrate (——) and the trihydrate monoperhydrate (–·–·).

Table 1. *Crystal data*

Space group $P\bar{1}$
$a = 7.35$ (2) Å
$b = 10.03$ (2)
$c = 10.24$ (2)
$\lambda(\mathrm{Cu}\ K\alpha_1) = 1.54051$ Å

$Z = 1$
$\alpha = 105.5$ (3)°
$\beta = 116.4$ (2)
$\gamma = 72.3$ (2)
$D_m = 1.47$ g cm^{-3}
$D_c = 1.50$

It should be noted that the salt tetrahydrate and the trihydrate monoperhydrate studied here are isomorphous.

Structure determination

The complete merged data of 1427 reflections were used to solve the structure with *MULTAN* 76 in space group $P\bar{1}$ [an $N(z)$ test showed a centric distribution] (Germain, Main & Woolfson, 1971) using molecular scattering factors in the generation of $|E|$ values. From an E map computed using the set of phases with the highest figure of merit all of the non-hydrogen atoms were located. Refinement was attempted firstly with isotropic and subsequently with anisotropic temperature factors. With $R = 0.17$ there was a lack of further convergence and for a number of atoms the thermal parameters became non-positive definite. It was considered that this might be due to some incompatibility between apparent temperature factors from the two data sets caused by different degrees of crystal perfection in the two sample batches.* Use of the second set of data allowed the refinement to proceed smoothly to a final R of 9·6%. In the last stages of the refinement the site occupancies of the peaks O(2) and

Table 2. *Fractional atomic coordinates and their standard deviations*

	x	y	z
C(1)	0·6904 (11)	0·9084 (7)	0·5384 (7)
C(2)	0·5155 (10)	0·8556 (7)	0·4386 (7)
C(3)	0·3214 (10)	0·9503 (7)	0·3984 (7)
C(21)	0·5366 (12)	0·7008 (7)	0·3781 (8)
O(21)	0·3936 (8)	0·6583 (5)	0·2678 (5)
O(22)	0·7065 (8)	0·6200 (5)	0·4460 (6)
C(31)	0·1225 (11)	0·9093 (7)	0·2894 (8)
O(31)	0·0244 (8)	0·8650 (5)	0·3392 (6)
O(32)	0·0556 (7)	0·9297 (5)	0·1630 (5)
C(11)	0·0865 (12)	0·6162 (8)	0·8531 (9)
N(11)	0·0358 (10)	0·5530 (8)	0·7134 (7)
N(12)	0·2430 (14)	0·5557 (8)	0·9582 (8)
N(13)	–0·0218 (12)	0·7435 (7)	0·8843 (8)
C(22)	0·6224 (12)	0·2670 (8)	0·3189 (9)
N(21)	0·6442 (11)	0·1251 (6)	0·2849 (8)
N(22)	0·4736 (11)	0·3468 (7)	0·2232 (8)
N(23)	0·7447 (11)	0·3246 (7)	0·4490 (7)
O(1)	0·6774 (8)	0·0301 (6)	0·9302 (6)
O(2)	0·2985 (15)	0·2398 (9)	0·9056 (9)
O(3)*	0·3678 (39)	0·2626 (18)	0·8537 (27)

* Site occupancy 0·38.

---

* The first set of data was collected with no special precaution to avoid the decomposition of the crystal and was consequently of a poorer standard than the second set, for which the crystal had been coated with varnish to avoid contact with atmospheric humidity. A refinement on this first data set alone could be forced as low as $R = 0.10$, but only at the expense of non-positive definite thermal parameters and poor bond lengths.

O(3) were allowed to refine and reached values of 1·0 and 0·4. An attempt at refinement in space group *P*1 showed no improvement in *R* and was accompanied by a deterioration in the standard deviations of the derived parameters.

The data were not corrected for absorption. Weighted refinement was not attempted (unit weights used throughout). Scattering factors were taken from *International Tables for X-ray Crystallography* (1974) and the XRAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) was used for the refinement. It did not prove possible to locate the H atoms. Final atomic positions are listed in Table 2 with bond lengths and angles in Table 3.* The structure is shown in Fig. 2. Details of the hydrogen bonds and of important planes are in Tables 4 and 5.

Discussion

The geometry of the guanidinium ions is normal (*e.g.* Adams & Pritchard, 1976). The pyromellitate anion is similar to that found in pyromellitic acid dihydrate (Takusagawa, Hirotsu & Shimada, 1969) except that the carboxyl C–O distances are equal in this salt and the dihedral angles between the carboxyl groups and the benzene ring are 15·9 and 84·5°, compared with the 21·4 and 74·5° found for the acid. These angles can of course vary in order to maximize the hydrogen bonding of the carboxyl groups, the energy for the rotation being comparable with that for hydrogen bond formation.

At the site of the water molecule, O(1), there is no evidence of substitution by hydrogen peroxide. Near the site of O(2), however, there was a small peak which refined to a site occupancy of 0·4. This has been interpreted as a statistical occupancy disorder with 60% of the sites occupied by water [*i.e.* 0·6 of O(2)] and 40% occupied by H_2O_2 [*i.e.* 0·4 of O(2) and the 0·4 occupancy at O(3)]. The stoichiometry is therefore close to the value: salt.$3H_2O.H_2O_2$. The only unusual feature of this interpretation is the bond length O(2)–O(3) which is extremely short at 1·0 Å. The most likely explanation of this fact is that the apparent position for the oxygen atom O(2) is made up of two contributions, one from a water oxygen and one from an H_2O_2 oxygen. Fig. 3 shows how such an interpretation would result in an apparently anomalously short peroxide O–O distance.

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

C(1)–C(2)	1·39 (1)	C(3)–C(2)–C(1)	118·3 (6)
C(2)–C(3)	1·40 (1)	C(2)–C(3)–C(1′)	119·3 (6)
C(3)–C(1′)	1·39 (1)		
C(21)–C(2)	1·49 (1)	C(1)–C(2)–C(21)	120·0 (5)
C(21)–O(21)	1·233 (8)	C(3)–C(2)–C(21)	121·6 (6)
C(21)–O(22)	1·269 (8)	C(2)–C(21)–O(21)	119·9 (5)
		C(2)–C(21)–O(22)	116·3 (5)
		O(21)–C(21)–O(22)	123·7 (7)
C(31)–C(3)	1·49 (1)	C(2)–C(3)–C(31)	123·9 (6)
C(31)–O(31)	1·27 (1)	C(1′)–C(3)–C(31)	116·6 (5)
C(31)–O(32)	1·21 (1)	C(3)–C(31)–O(31)	116·7 (7)
		C(3)–C(31)–O(32)	119·1 (9)
		O(31)–C(31)–O(32)	123·8 (7)
C(11)–N(11)	1·33 (1)	N(11)–C(11)–N(12)	120·6 (7)
C(11)–N(12)	1·29 (1)	N(11)–C(11)–N(13)	119·6 (6)
C(11)–N(13)	1·32 (1)	N(12)–C(11)–N(13)	119·7 (7)
C(22)–N(21)	1·34 (1)	N(21)–C(22)–N(22)	118·9 (6)
C(22)–N(22)	1·31 (1)	N(21)–C(22)–N(23)	120·1 (7)
C(22)–N(23)	1·32 (1)	N(22)–C(22)–N(23)	120·8 (7)
O(2)–O(3)	0·98 (3)		

N.B. Site occupancy of O(3) is 0·38.

Table 4. *Hydrogen-bonding geometry* (Å)

N(11)···O(22^{i})	2·81 (1)	N(22)···O(2^{vii})	2·93 (1)
N(11)···O(22^{ii})	2·91 (1)	N(23)···O(22)	2·89 (1)
N(12)···O(21^{iii})	2·85 (1)	N(23)···O(31^{ii})	2·85 (1)
N(12)···O(3)	2·86 (2)	O(1)···O(32^{ii})	2·69 (1)
N(12)···O(2)	3·00 (2)	O(1)···O(32^{viii})	2·84 (1)
N(13)···O(32^{iii})	2·88 (1)	O(1)···O(3)	2·71 (2)
N(13)···O(1^{iv})	3·11 (1)	O(2)···O(31^{ix})	2·80 (2)
N(21)···O(1^{v})	2·93 (1)	O(2)···O(1)	2·89 (1)
N(21)···O(31^{vi})	3·14 (1)	O(3)···O(21^{ii})	2·92 (2)
N(22)···O(21)	2·94 (1)		

Symmetry code

(i) $-1 + x, y, z$
(ii) $1 - x, 1 - y, 1 - z$
(iii) $x, y, 1 + z$
(iv) $-1 + x, 1 + y, z$
(v) $1 - x, -y, 1 - z$
(vi) $1 + x, -1 + y, z$
(vii) $x, y, -1 + z$
(viii) $1 + x, -1 + y, 1 + z$
(ix) $-x, 1 - y, 1 - z$

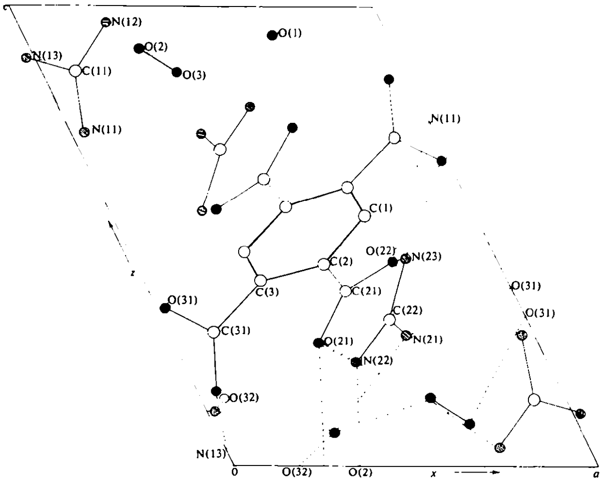

Fig. 2. Projection of the structure along the *b* axis.

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33573 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 5. *Least-squares planes* (*in direct space*) *and deviations of atoms* (Å) *from them*

(*a*) Benzene ring. Plane through C(1), C(2) and C(3) plus the atoms generated through the centre of symmetry at ($\frac{1}{2}$,0,$\frac{1}{2}$)

$$-4{\cdot}2938x - 4{\cdot}7127y + 9{\cdot}9024z = -1{\cdot}9084$$

C(1)	−0·006
C(2)	0·006
C(3)	−0·006

(*b*) Carboxyl group defined by C(2), C(21), O(21), O(22)

$$-5{\cdot}7558x - 4{\cdot}3798y + 9{\cdot}1653z = -2{\cdot}6942$$

C(2)	0·000	O(21)	−0·001
C(21)	0·001	O(22)	0·000

(*c*) Carboxyl group defined by C(3), C(31), O(31), O(32)

$$-2{\cdot}6489x + 7{\cdot}5741y + 2{\cdot}3072z = 7{\cdot}2598$$

C(3)	0·008	O(31)	0·010
C(31)	−0·029	O(32)	0·010

(*d*) Guanidinium ion defined by C(11), N(11), N(12), N(13)

$$6{\cdot}522x + 6{\cdot}998y - 5{\cdot}598z = 0{\cdot}107$$

C(11)	−0·007	N(12)	0·002
N(11)	0·002	N(13)	0·002

(*e*) Guanidinium ion defined by C(22), N(21), N(22), N(23)

$$-6{\cdot}744x - 3{\cdot}017y + 7{\cdot}800z = -2{\cdot}504$$

C(22)	−0·012	N(22)	0·004
N(21)	0·004	N(23)	0·004

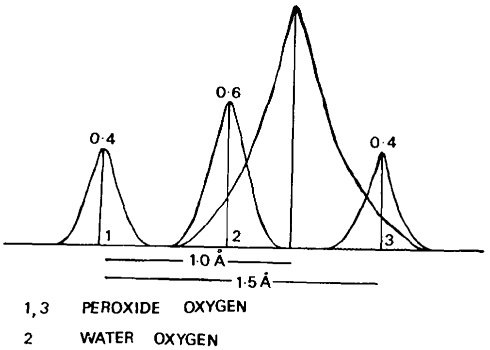

Fig. 3. The effect of partial site occupancy by water and H_2O_2 on the apparent O—O bond distance of the hydrogen peroxide.

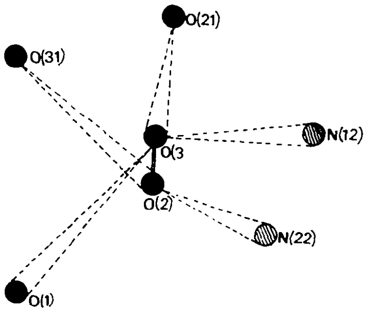

Fig. 4. The hydrogen-bonding scheme of the hydrogen peroxide molecule.

The hydrogen-bonding scheme is three-dimensional: all guanidinium H atoms are involved in hydrogen bonds (see Fig. 2, Table 4). Two possible situations arise. Firstly, when the partly occupied sites are filled with water, O(1) receives two hydrogen bonds from guanidinium hydrogen atoms [and also possibly one from O(2)] while donating two hydrogen bonds to $O(32^{ii})$ and $O(32^{viii})$. O(2) receives two hydrogen bonds from guanidinium groups and donates two bonds to O(1) and $O(31^{ix})$. Secondly, when the partially occupied sites are filled with H_2O_2, O(1) receives two hydrogen bonds from guanidinium ions and donates two such bonds [there are three close contacts to $O(32^{ii})$, $O(32^{viii})$ and O(3)]. O(2) accepts a hydrogen bond from a guanidinium hydrogen and donates one to $O(31^{ix})$, whereas O(3) donates one hydrogen to $O(21^{ii})$ and accepts two hydrogen bonds from O(1) and N(12). The hydrogen peroxide group, then, donates two hydrogen bonds and receives three (see Fig. 4). This type of scheme has been seen in the related perhydrate, guanidinium pyrophosphate sesquihydrate monoperhydrate (Adams & Ramdas, 1978), whereas in the series of alkali-metal oxalate perhydrates of Pedersen (1967, 1969, 1972*a*,*b*) and Pedersen & Pedersen (1964) the hydrogen peroxide molecules only accept two hydrogen bonds.

It may be noted that in the extremely stable perhydrate formed by urea, each H_2O_2 molecule accepts four hydrogen bonds (Lu, Hughes & Giguère, 1941). However, there may not always be a direct relationship between hydrogen-bond formation and stability for perhydrates since in the relatively unstable alkali-metal oxalate perhydrates the hydrogen bonds are stronger (as evidenced by bond lengths) than those in the adduct $4Na_2SO_4.2H_2O_2.NaCl$ (Adams & Pritchard, 1978) which is extremely stable.

We thank Professor J. M. Thomas, FRS for his encouragement and Unilever Ltd for their support.

References

Adams, J. M. & Pritchard, R. G. (1976). *Acta Cryst.* B**32**, 2438–2440.

Adams, J. M. & Pritchard, R. G. (1978). *Acta Cryst.* B**34**, 1428–1432.

Adams, J. M., Pritchard, R. G. & Thomas, J. M. (1976). *J. Chem. Soc. Chem. Commun.* pp. 358–359.

Adams, J. M. & Ramdas, V. (1978). *Acta Cryst.* B**34**, 2150–2156.

Germain, G., Main, P. & Woolfson, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Lu, C. S., Hughes, E. W. & Giguère, P. A. (1941). *J. Am. Chem. Soc.* **63**, 1507–1513.

PEDERSEN, B. F. (1967). *Acta Chem. Scand.* **21**, 801–811.
PEDERSEN, B. F. (1969). *Acta Chem. Scand.* **23**, 1871–1877.
PEDERSEN, B. F. (1972*a*). *Acta Cryst.* B**28**, 746–754.
PEDERSEN, B. F. (1972*b*). *Acta Cryst.* B**28**, 1014–1016.
PEDERSEN, B. F. & PEDERSEN, B. (1964). *Acta Chem. Scand.* **18**, 1454–1468.
STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1972). The XRAY system – version of June 1972. Update of April 1974. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.
TAKUSAGAWA, F., HIROTSU, K. & SHIMADA, A. (1969). *Bull. Chem. Soc. Jpn*, **42**, 3368.

Acta Cryst. (1978). B**34**, 2785–2789

A Reinvestigation on Benzalazine, Influence of TDS and Comparison with Different Experiments*

BY V. MOM† AND G. DE WITH‡

Chemical Physics Laboratory, Twente University of Technology, PO Box 217, Enschede, The Netherlands

(*Received* 3 *February* 1978; *accepted* 28 *April* 1978)

The structure of benzalazine (dibenzylhydrazine, benzylideneazine, $C_{14}H_{12}N_2$) was redetermined at 165 K by means of X-ray methods. The influence of thermal diffuse scattering (TDS) on the structure and temperature factors was found to be small. A comparison with the results of other experiments was made.

Introduction

The influence of the thermal diffuse scattering (TDS) correction on the determination of positional and thermal parameters and the electron distribution is one of the topics in accurate X-ray crystallography. For this kind of work, benzalazine seems a suitable compound since the elastic constants are known (Haussühl, 1965). In this paper only the influence of TDS on the determination of positional and thermal parameters is examined because the experiment did not appear to be accurate enough to study the influence on the determination of charge distribution.

Three earlier X-ray experiments have been performed on benzalazine (Sinha, 1970; Kobayashi, Ogawa & Shintani, 1969; Burke-Laing & Laing, 1976). This gives an opportunity to compare the results of different experiments on the same compound.

Experimental

Benzalazine crystals were grown from a saturated mixture of ethanol and chloroform (ratio 1:1) at 293 K, with an initial evaporation rate of about 10% solvent per hour. A single crystal of dimensions 0·10 × 0·15 × 0·43 mm was selected and mounted on a Philips PW1100 computer-controlled four-circle diffractometer [Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å, flat graphite monochromator, scintillation counter, pulse-height discriminator, Leyboldt Heraeus NCD1 cooling device (Hornstra & Vossers, 1973)]. Measurements were performed at 165 ± 1 K.

Reflexions were measured through the whole sphere up to $s = \sin\theta/\lambda = 0{\cdot}7$ Å^{-1} ($\theta = 30°$). The $\omega/2\theta$ step-scanning technique at a rate of 0·05° s^{-1}, a step size of 0·02° and a scan width of 2·0° were used. The detector aperture was chosen as 2·0° horizontally and 1·5° vertically. Unit-cell information is given in Table 1. Cell constants were calculated from the data given by Mom & de With (1978).

Data treatment

During the measurements the three reference reflexions showed only small random fluctuations. Consequently, no rescaling of measured data was performed. The

Table 1. *General unit-cell information*

Here and in the following tables (least-squares) standard deviations are given in parentheses.

a	13·051 (2) Å	*V*	1128·9 (7) Å^3
b	11·703 (4)	Space group	*Pbcn*
c	7·391 (1)	*Z*	4
		μ(Mo $K\alpha$)	0·685 cm^{-1}

---

* This research has been carried out under auspices of the Foundation for Fundamental Research on Matter by Electrons and X-rays (FOMRE) and with aid from the Netherlands Organization for Advancement of Pure Research (ZWO).

† Present address: Gorlaeus Laboratory, University of Leiden, PO Box 75, Leiden, The Netherlands.

‡ To whom correspondence should be addressed. Present address: Philips Research Laboratories, Eindhoven, The Netherlands.