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

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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}

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effective scan volume was determined from the step-scan profiles according to the algorithm of Larsen & Lehmann (1974). Allowance was made for unequal left and right background, originally not contained in the algorithm. Moreover, the width of the peak was taken somewhat larger than the calculated one to prevent systematic errors. Net intensities were calculated accordingly.

Absorption was corrected with the program *ACXR* (Harkema, 1976). Negligible corrections emerged from the calculation and the uncorrected data were used for further analysis.

Corrections for first-order TDS were applied according to: $I_B = I_o/(1 + \alpha)$ (see *e.g.*, Harada & Sakata, 1974; Cochran, 1969). I_B represents the 'true' Bragg intensity and I_o the measured intensity. The TDS correction factor α has been calculated (de With, Harkema & Feil, 1976) in the 'long-wave' approximation. The elastic constants, measured at 293 K, were extrapolated linearly to 165 K (Haussühl, 1965) (Table 2).

Each independent reflexion was measured approximately ten times (including those symmetry related). From the different measurements for each reflexion a weighted average was calculated. The weights used in averaging were chosen as inverse counting statistics variances.

The total number of independent reflexions was 1664 of which 1090 had intensities of at least twice their counting-statistics standard deviation.

An internal consistency index R_I, defined as $R_I = \sum_{i,j} (I_{ij} - \bar{I}_j)/\sum_{i,j} I_{ij}$ was calculated. $\sum_j$ extends over all independent reflexions and $\sum_i$ over all equivalent reflexions. I_{ij} is the measured intensity and $\bar{I}_j$ the corresponding weighted average. R_I was 6·6% before as well as after TDS correction.

Variances of reflexions were calculated according to the procedure proposed by McCandlish, Stout & Andrews (1975). They derived the following formula: $\sigma^2(I) = K^2T + S^2(K)I_o^2 + K^2P^2I_o^2$ where I is the real net intensity, T the total number of counts, I_o the observed net intensity, K the scaling factor ($I = KI_o$; in this case K is always 1·0), $S^2(K)$ the variance of K and P the instability constant. P was calculated* from the three reference reflexions ($P1 = 2{\cdot}6 \times 10^{-3}$, $P2 = 7{\cdot}4 \times 10^{-3}$, $P3 = 2{\cdot}6 \times 10^{-3}$), resulting in an average P value of $4{\cdot}2 \times 10^{-3}$. [Compare the P values for this diffractometer reported earlier: $P = 2{\cdot}8 \times 10^{-3}$ (de With & Feil, 1976) and $P = 3{\cdot}1 \times 10^{-3}$ (de With & Harkema, 1977).]

The variance of K showed no systematic time dependence owing to the consistent behaviour of the reference reflexions. Therefore an average value was used [$S^2(K) = 1{\cdot}3 \times 10^{-3}$]. Now $S^2(K)I_o^2$ and $K^2P^2I_o^2$ can be taken together: $[S^2(K) + K^2P^2]^{1/2} = 3{\cdot}6 \times 10^{-2}$; this value is directly comparable with that of N in the weighting scheme often used: $\sigma^2(I) = T + N^2I_o^2$, with N typically chosen between $1{\cdot}0 \times 10^{-2}$ and $5{\cdot}0 \times 10^{-2}$.

Table 2. *Elastic constants of benzalazine at* 165 K *in* Mbar (10^{12} dyne cm^{-1})

Values are calculated from the elastic constants and their temperature coefficients as measured by Haussühl (1965) at 293 K.

0·1800	0·0666	0·0390	0	0	0
	0·1040	0·0663	0	0	0
		0·0843	0	0	0
			0·0272	0	0
				0·0132	0
					0·0429

Lorentz–polarization and monochromator corrections [for an ideal mosaic monochromator crystal (Azaroff, 1955)] were performed. A normal distribution in the structure factor F was assumed to calculate $\sigma(F)$ from $\sigma(I)$ (Rees, 1976).*

Refinements

Full-matrix least-squares refinements have been carried out by a modification of *ORFLS* (Busing, Martin & Levy, 1962). The function minimized was $\sum w(|F_o| - k|F_c|)^2$, k being a scale factor, $|F_o|$ the observed structure factor and $|F_c|$ the calculated structure factor. The weight w for each reflexion was taken to be σ^{-2} where σ is the standard deviation of $|F_o|$. The summation is over all independent reflexions (Hirshfeld & Rabinovich, 1973).

The data as given by Burke-Laing & Laing (1976) served as starting parameters. Atomic scattering factors for the C and N atoms were taken from *International Tables for X-ray Crystallography* (1974). For the H atoms the scattering factor given by Stewart, Davidson & Simpson (1965) was used. The introduction of an isotropic secondary extinction factor (Larson, 1969) gave no significant improvement. The value of the extinction parameter was very small. Therefore the correction has been omitted in the subsequent analysis.

Relevant information about the refinements is given in Table 3. Final coordinates and temperature factors are given in the supplementary publication.

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* $P = \{[s^2(\bar{I}) - \bar{I}]/\bar{I}^2\}^{1/2}$, with $s^2(\bar{I}) = \sum(I - \bar{I})^2/N \times (N - 1)$ where $\bar{I}$ is the average reference-reflexion intensity and N the number of reference reflexions. However, McCandlish *et al.* (1975) calculated P with $s^2(I) = \sum (I - \bar{I})^2/N$.

* Lists of structure factors, final coordinates and temperature factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33582 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Results and discussion

Bond distances and angles were derived from the positional parameters with *ORFFE* (Busing, Martin & Levy, 1964), and are given for the non-hydrogen atoms in Table 4. The numbering is according to Fig. 1. As observed before (de With, Harkema & Feil, 1976) the derived bond distances and angles are unaffected by the TDS correction.

The root-mean-square displacements (r.m.s.d.'s) along the principal axes for the heavy atoms are given in Table 5. As compared with pyrazine (de With, Harkema & Feil, 1976), where the influence of TDS correction on the r.m.s.d.'s is also approximately known, the influence is rather small (about one standard deviation). This may be partly due to the much smaller scan volume for the reflexions.

A rigid-bond test, as discussed by Hirshfeld (1976), was performed. The r.m.s.d.'s along the bonds, derived from data not corrected for TDS, are given in Table 6. The average difference is 0·9 times the combined standard deviations. Very similar results are obtained from the data corrected for TDS.

A least-squares plane was fitted through the positional parameters of the phenyl ring. Its intercept equation is given by $-59{\cdot}19X + 146{\cdot}5Y + 164{\cdot}4Z = 1$ where X, Y and Z are the fractional coordinates along the crystal axes. The χ^2 value obtained is 9·8 ($\chi^2 = \sum_m d_m^2/\sigma_m^2$, where d_m is the distance of atom m to the plane and σ_m the corresponding standard deviation).

Table 3. *Refinement information*

(No) TDS = (No) TDS correction performed; FA = full-angle refinement; $R = \sum \Delta F/\sum F_o$; $R_w = (\sum w\Delta F^2/\sum wF_o^2)^{1/2}$; $S = [\sum w\Delta F^2/(n - m)]^{1/2}$; $\Delta F = |F_o - F_c|$; $w = 1/\sigma^2(F_o)$; n = number of reflexions; m = number of parameters; n_s = number of significant reflexions $[I_o > 2\sigma(I_o)]$.

		R	R_w	S	Scale	n	n_s
TDS	FA	11·0	7·4	1·79	1·258 (5)	1664	1090
No TDS	FA	11·0	7·2	1·76	1·251 (5)	1664	1090
No TDS	0·0–0·6 Å^{-1}	7·2	5·9	1·83	1·265 (5)	1023	790
No TDS	Significant reflexions only	6·9	6·8	2·08	1·257 (6)	–	–

Table 4. *Bond distances* (Å) *and angles* (°) *for non-hydrogen atoms, corrected for TDS* (*left*), *not corrected for TDS* (*right*)

N–N	1·4179 (29)	1·4180 (29)
N–C(1)	1·2745 (27)	1·2749 (27)
C(1)–C(2)	1·4668 (27)	1·4663 (27)
C(2)–C(3)	1·3888 (27)	1·3888 (27)
C(3)–C(4)	1·3828 (31)	1·3813 (31)
C(4)–C(5)	1·3794 (32)	1·3791 (32)
C(5)–C(6)	1·3772 (32)	1·3766 (32)
C(6)–C(7)	1·3797 (30)	1·3806 (30)
C(7)–C(2)	1·3897 (27)	1·3892 (27)
N–N–C(1)	111·75 (22)	111·73 (21)
N–C(1)–C(2)	121·92 (19)	121·91 (19)
C(1)–C(2)–C(3)	119·23 (19)	119·27 (19)
C(1)–C(2)–C(7)	121·35 (18)	121·33 (18)
C(3)–C(2)–C(7)	119·41 (20)	119·39 (19)
C(2)–C(3)–C(4)	120·36 (21)	120·37 (21)
C(3)–C(4)–C(5)	119·73 (22)	119·68 (21)
C(4)–C(5)–C(6)	120·37 (21)	120·42 (21)
C(5)–C(6)–C(7)	120·20 (22)	120·18 (22)
C(6)–C(7)–C(2)	119·99 (21)	119·96 (21)

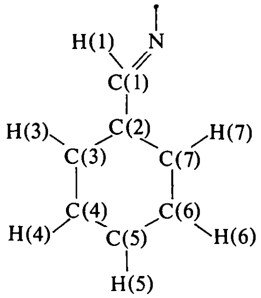

Fig. 1. Atomic numbering of benzalazine.

Table 6. *Root-mean-square displacements along the bonds* (Å)

$z_{A,B}$ denotes the r.m.s.d. of atom A along the vector from atom A to atom B. The standard deviation in all r.m.s.d.'s is 0·003 Å.

A	B	$z_{A,B}$	$z_{B,A}$
N	C(1)	0·199	0·204
C(1)	C(2)	0·203	0·196
C(2)	C(3)	0·197	0·197
C(3)	C(4)	0·217	0·219
C(4)	C(5)	0·233	0·230
C(5)	C(6)	0·229	0·234
C(6)	C(7)	0·212	0·209
C(7)	C(2)	0·189	0·184

Table 5. *Root-mean-square displacements* (Å) *along the principal axes*

	TDS			No TDS		
	u_1	u_2	u_3	u_1	u_2	u_3
N	0·188 (2)	0·200 (3)	0·208 (3)	0·184 (2)	0·198 (3)	0·205 (3)
C(1)	0·180 (3)	0·185 (3)	0·215 (3)	0·177 (3)	0·182 (3)	0·211 (3)
C(2)	0·160 (3)	0·180 (3)	0·205 (3)	0·156 (4)	0·184 (3)	0·202 (3)
C(3)	0·185 (3)	0·195 (3)	0·231 (3)	0·183 (3)	0·191 (3)	0·227 (3)
C(4)	0·185 (3)	0·228 (3)	0·242 (3)	0·182 (3)	0·225 (3)	0·240 (3)
C(5)	0·191 (3)	0·220 (3)	0·246 (3)	0·188 (3)	0·217 (3)	0·243 (3)
C(6)	0·195 (3)	0·210 (3)	0·239 (3)	0·192 (3)	0·208 (3)	0·237 (3)
C(7)	0·188 (3)	0·191 (3)	0·214 (3)	0·184 (3)	0·188 (3)	0·211 (3)

Expected χ^2 values are: $\chi^2_{3,0\cdot025} = 9\cdot4$ and $\chi^2_{3,0\cdot01} = 11\cdot3$. The deviations of the heavy atoms from the plane are given in Table 7. Atoms N and C(1) are significantly out of the plane.

Comparison of results of different experiments

The differences between the results derived from the various experiments have been tested in two different ways: a χ^2 test and a half normal probability plot (h.n.p. plot).

Our experiment was done at 165 K while the other experiments were done at 293 K. A small difference in orientation due to this difference in temperature spoils tests on fractional coordinates. Therefore the bond lengths and angles (of the non-hydrogen atoms) were used for the tests. The bond lengths and angles and corresponding standard deviations were calculated from the fractional coordinates and their standard deviations as given by the different authors. Relevant information on the various experiments is given in Table 8.

In the χ^2 test (Hamilton, 1969) the quantity $\delta^2 p = \sum_{i=1}^{N} \delta^2 p_i$ is calculated. δp_i is given by $\delta p_i = \Delta p_i / \sigma(\Delta p_i)$ in which Δp_i is the difference between two corresponding parameters in two data sets and $\sigma(\Delta p_i)$ is the standard deviation of this difference. The resulting $\delta^2 p$ can be tested against χ^2 with N degrees of freedom at different levels of significance. This provides us with an indication as to whether the differences found are drawn from a normal distribution with unit variance and zero means (standard normal distribution). Therefore when the calculated value of $\delta^2 p$ exceeds the expected value of $\chi^2_{N,\alpha}$, it may be concluded that the two data sets are significantly different at the 100α% significance level. The results are given in Table 9. Only experiments 2 and 4 differ significantly. The bond lengths as derived in this work (experiment 4) are all systematically longer. In view of the lower temperature this is not surprising. The fact that no significant differences are found between the results derived from the two other data sets and this work is largely due to the high standard deviations of the data in these sets.

Secondly, the δp_i distributions have been analysed by means of h.n.p. plots (Abrahams & Keve, 1971). The δp_i are ordered in increasing magnitude and plotted against the expected quantiles for a half-normal distribution. For small samples (up to 41) the expected quantiles are tabulated (Hamilton & Abrahams, 1972). The resulting plot is a straight line of unit slope and zero intercept when the distribution of the δp_i is normal. A straight line was least-squares fitted through the points of the plots. The resulting slopes and intercepts are given in Table 10. The results of the h.n.p.-plot analysis more or less confirm the results of the χ^2 test.

Table 7. *Deviations of the atoms from the least-squares plane of the phenyl ring* (Å)

N	−0·0094 (14)		
C(1)	−0·0321 (17)	H(1)	−0·022 (17)
C(2)	−0·0006 (15)		
C(3)	0·0021 (18)	H(3)	0·026 (17)
C(4)	−0·0005 (19)	H(4)	0·050 (21)
C(5)	−0·0026 (19)	H(5)	0·009 (17)
C(6)	0·0041 (20)	H(6)	−0·003 (19)
C(7)	−0·0025 (17)	H(7)	−0·055 (16)

Table 9. *Bond-length results*

Combination[a]		χ^2 obtained	Slope	Intercept	Correlation coefficient
1	2	5·0	0·76 (4)	−0·10 (4)	0·99
1	3	10·6	1·37 (13)	−0·32 (13)	0·97
1	4	8·7	1·13 (7)	−0·13 (7)	0·99
2	3	12·8	1·60 (15)	−0·45 (14)	0·97
2	4	24·6	1·47 (24)	0·25 (23)	0·92
3	4	13·3	1·19 (24)	−0·48 (23)	0·93

$\chi^2_{9,0\cdot05} = 16\cdot9$ $\chi^2_{9,0\cdot01} = 21\cdot7$.

(*a*) For numbering see Table 8.

Table 8. *Reference information for the different experiments*

Experiment	1	2	3	4
Radiation	Cu *Kα*	Mo *Kα*	Cu *Kα*	Mo *Kα*
R (%)	11·8[a]	4·7[b]	15·9[c]	11·0[a]
Number of reflexions	851	733[b]	212	1664[a]
$\sin\theta_{\max}/\lambda$ (Å^{-1})	–	0·6	–	0·7
Method	film	PW1100 diffractometer	film	PW1100 diffractometer
Absorption correction	no	no	no	no
Extinction correction	no	skipped reflexions 002, 121, 200, 020	no	no
Temperature (K)	293	293	293	165

(1) Kobayashi, Ogawa & Shintani (1969). (2) Burke-Laing & Laing (1976). (3) Sinha (1970). (4) This work.

(*a*) Including all reflexions. (*b*) Including only reflexions with $I > 1\cdot65\sigma(I)$. (*c*) Average of the *hk*0, *h*0*l* and 0*kl* planes.

Table 10. *Angle results*

Combination[a]		χ^2 obtained	Slope	Intercept	Correlation coefficient
1	2	10·9	1·22 (11)	−0·17 (10)	0·97
1	3	13·1	1·48 (15)	−0·39 (15)	0·96
1	4	5·9	0·87 (8)	−0·10 (7)	0·97
2	3	8·3	0·92 (8)	−0·02 (8)	0·97
2	4	34·0	1·85 (7)	0·08 (7)	0·99
3	4	15·1	1·39 (11)	−0·14 (11)	0·97

$\chi^2_{10,0\cdot05} = 18\cdot3$ $\chi^2_{10,0\cdot01} = 23\cdot2$

(*a*) For numbering see Table 8.

Conclusions

Derived bond distances and angles are unaffected by TDS correction. The influence of the TDS correction on the r.m.s.d.'s is rather small. The phenyl ring of benzalazine is planar while the atoms C(1) and N are significantly out of this plane. The structure determined in this work (165 K) is significantly different from the structure determined at room temperature.

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A Simple Refinement of Density Distributions of Bonding Electrons.

IX. Bond Electron Density Distribution in Thiourea, $CS(NH_2)_2$, at 123 K

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A model for thiourea is described in which valence electrons are included separately in the refinement. A significantly better R value is obtained for this model (0·017) compared with the usual spherical atom refinement (0·025). Core parameters agree within 2·5σ with those from the neutron diffraction study [Elcombe & Taylor (1968). *Acta Cryst.* A**24**, 410–420]. Bond population parameters are given, and a dynamic valence density based on the refined model is presented. This density is compared with the valence density of urea [Mullen & Hellner (1978). *Acta Cryst.* B**34**, 1624–1627].