Crystal structure of 4,6-dinitro-1-(5-tetrazolyl)-1*H*-indazole trihydrate

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Abstract

The title compound, $C_8H_4N_8O_4 \cdot 3H_2O$, crystallizes in space group $P\bar{1}$ with cell constants $a = 7.022(1)$, $b = 9.507(2)$, $c = 10.906(2)$ Å, $\alpha = 84.99(1)$, $\beta = 71.89(1)$, $\gamma = 72.56(1)°$, $Z = 2$, and $V_c = 660.2$ Å^3. The structure was solved by direct methods using diffractometer data and was refined by full-matrix least-squares methods to an R value of 0.060 for 2112 observed reflections. The molecule, consisting of a phenyl ring fused to a pyrazole ring with a tetrazole ring connected to it equatorially, is planar except for the N(7) nitro-group oxygen atoms. The structure is stabilized by a three-dimensional network of O–H $\cdots$ O, O–H $\cdots$ N, and N–H $\cdots$ O hydrogen bonds through the water molecules.

Introduction

The compound 2,4,6-trinitrobenzaldehyde-1*H*(2*H*)-tetrazol-5-yl-hydrazone used in the preparation of explosives, is obtained by the reaction of 5-hydrazinotetrazole hydrochloride in aqueous solution with 2,4,6-trinitrobenzaldehyde in alcohol (Om Reddy *et al.*, 1981) and is usually recrystallized from dimethyl formamide solution. The structure proposed on the basis of analytical studies using UV, IR, NMR, and mass spectrophotometric
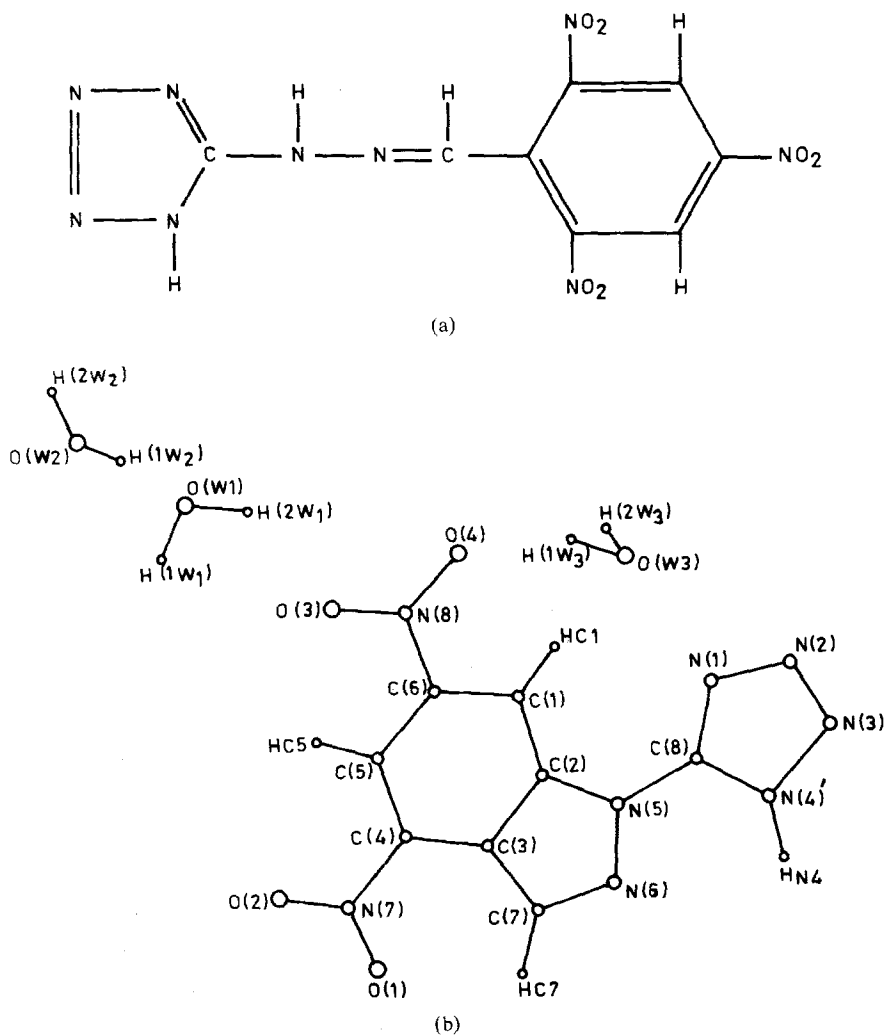
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(a)

(b)

Fig. 1. (a) 2,4,6-Trinitrobenzaldehyde-1H(2H)-tetrazol-5-yl hydrazone molecule; (b) 4,6-dinitro-1-(5-tetrazolyl)-1H-indazole trihydrate molecule.

techniques is shown in Fig. 1a. Thermal studies on several tetrazole derivatives using a differential scanning calorimeter have indicated that the reactivity of these compounds increases with increasing number of nitro groups in the phenyl ring (Om Reddy et al., 1981). However, the structure obtained during this crystal structure analysis using single crystal X-ray diffraction revealed the absence of one of the nitro groups, the presence of

three water molecules, and the cyclization of the compound (Fig. 1b). Since the compound was recrystallized from a boiling dimethyl formamide solution, it is postulated that the three nitro groups and the one azomethine function deactivated the benzene ring by their electron-withdrawing power, resulting in an intramolecular nucleophilic substitution. The carbanion created by the attack of the nitrogen lone pair was stabilized by the electron-withdrawing groups, and the elimination of the nitro group restored the aromaticity, forming a stable indazole system. The compound investigated is now known to be 4,6-dinitro-1-(5-tetrazolyl)-1H-indazole trihydrate. No such change has been observed in the study of 2,4-dinitrobenzaldehyde-1H(2H)-tetrazol-5-yl-hydrazone (Sake Gowda *et al.*, 1982). The present work deals with the elucidation of the crystal and molecular structure of the former compound and the nature of the hydrogen-bonding scheme.

Experimental

Single crystals, brownish in color, were obtained from A. K. Chatterjee and G. Om Reddy of IDL Chemicals Ltd., Hyderabad, India. A single crystal of dimensions 0.13 × 0.16 × 0.20 mm was used for data collection. Preliminary data of the compound indicated that the crystals belong to triclinic space group $P\bar{1}$ (No. 2) with two molecules in the unit cell. Accurate cell parameters were obtained from least-squares refinement of 20 reflections from a crystal mounted on a Syntex $P2_1$-F diffractometer using nickel-filtered Cu $K\alpha_1$ radiation. The density of the crystal was measured by the flotation technique using chlorobenzene and methyl iodide. The crystal data are given in Table 1.

Table 1. Crystal data

Chemical formula	C₈H₄N₈O₄·3H₂O
Molecular weight	330.23
Crystal system	Triclinic
Space Group	$P\bar{1}$ (No. 2)
Z	2
a	7.022(1) Å
b	9.507(2)
c	10.906(2)
α	84.99(1)°
β	71.89(1)
γ	72.56(1)
$F(000)$	340
V_c	660.17 Å³
λ(Cu $K\alpha_1$)	1.54051 Å
μ(Cu $K\alpha_1$)	1.16 mm⁻¹
D_x	1.66 g cm⁻³
D_m	1.62 g cm⁻³

The three-dimensional intensity data were collected using the θ–2θ scan technique in the 2θ range $0 \leq 2\theta \leq 130°$. A total of 2433 reflections were measured. Three check reflections monitored every 102 reflections indicated no appreciable variation in the intensity spread during the course of data collection. The crystal was recentered automatically every 633 reflections. Of 2239 independent reflections, 2112 reflections with $I \geq 2\sigma(I)$ were treated as observed. The data were corrected for Lorentz and polarization effects; no decay or absorption corrections were applied.

Structure determination and refinement

The structure was solved by direct methods using MULTAN (Main *et al.*, 1978) with 192 largest normalized structure factors having $|E_{min}| \geq 1.30$ and 50 smallest E values with $|E_{max}| = 0.20$. All the nonhydrogen atoms were located from the E map computed for these data with the phase set having the highest combined figure of merit. The presence of three water molecules of crystallization was confirmed from the appearance of three heavy peaks in successive difference Fourier maps.

The structure was refined with isotropic temperature factors by a full-matrix least-squares method using the SHELX (Sheldrick, 1976) program incorporated in the DEC-1090 computer system at the Indian Institute of Science (IISc), Bangalore, India, resulting in an R value of 15%. Further refinement with anisotropic temperature factors reduced the R factor to 8%. All the hydrogen atoms except the tetrazole hydrogen were located from the difference Fourier map. The tetrazole hydrogen was fixed at N(4) using stereochemical considerations to account for its intermolecular contact with O(W3). The positional and thermal parameters of all the hydrogen atoms except H(N4) and H(2W3) were refined. The refinement was terminated when the maximum shift/esd was 0.25. The final unweighted and weighted residuals are 0.060 and 0.087, respectively. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $w = K/(\sigma^2(F_o) + |g|F_o^2)$, $K = 1.00$, $g = 0.0396$, with σ based on counting statistics. The atomic scattering factors for C, N, and O are taken from Cromer and Mann (1968), and those for hydrogen from Stewart *et al.* (1965). The data reduction and MULTAN programs were from the Adelphi University Syntex XTL and Burroughs 6800 crystallographic programs; all other programs used in this study were from the IISc crystallographic library. The final positional parameters of nonhydrogen atoms with B_{eq} are given in Table 2. The positional and thermal parameters of hydrogen atoms are given in Table 3.

Table 2. Final positional parameters ($\times$ 10^4) for nonhydrogen atoms with esd's in parentheses

Atom	x	y	z	$B_{eq}{}^a$
C(1)	139(3)	1196(3)	7231(3)	2.61(09)
C(2)	−119(3)	−187(2)	7592(2)	2.41(08)
C(3)	846(3)	−1419(2)	6771(2)	2.50(06)
C(4)	2148(3)	−1222(2)	5536(2)	2.42(06)
C(5)	2469(3)	107(3)	5131(2)	2.83(07)
C(6)	1424(3)	1306(2)	6000(2)	2.60(06)
C(7)	199(3)	−2592(3)	7489(2)	2.90(06)
C(8)	−2434(3)	90(2)	9887(2)	2.28(05)
N(1)	−2773(3)	1518(2)	10058(2)	3.09(06)
N(2)	−3982(3)	1750(2)	11293(2)	3.09(05)
N(3)	−4342(3)	546(2)	11802(2)	3.10(05)
N(4)	−3348(3)	−554(2)	10929(2)	2.81(05)
N(5)	−1223(3)	−676(2)	8736(2)	2.52(05)
N(6)	−1021(3)	−2145(2)	8666(2)	3.07(05)
N(7)	3186(3)	−2472(2)	4642(2)	3.07(06)
N(8)	1734(3)	2752(2)	5579(2)	3.39(06)
O(1)	2708(4)	−3608(2)	4950(2)	5.10(10)
O(2)	4416(3)	−2289(2)	3612(2)	4.68(09)
O(3)	2870(3)	2835(2)	4490(2)	5.21(13)
O(4)	869(3)	3786(2)	6338(2)	4.80(09)
O(W1)	4455(3)	4616(2)	2363(2)	4.17(07)
O(W2)	1908(3)	5709(2)	791(2)	3.88(04)
O(W3)	2615(3)	3694(2)	8804(2)	4.70(05)

$^a B_{eq}$ is the arithmetic mean of the principal axes of thermal ellipsoids.

Table 3. Positional parameters ($\times$ 10^3) for hydrogen atoms with B_{iso} (eds's in parentheses)

Atom	x	y	z	B_{iso}
H(C1)	−53(4)	205(3)	773(3)	2.3(4)
H(C5)	339(4)	46(3)	429(3)	3.4(6)
H(C7)	79(4)	−365(4)	724(3)	3.4(5)
H(N4)^a	343	157	883	3.3
H(1W1)	501(4)	360(4)	205(3)	4.8(6)
H(2W1)	389(5)	447(4)	332(4)	5.7(7)
H(1W2)	264(6)	537(4)	148(4)	7.6(9)
H(2W2)	224(4)	663(4)	48(3)	4.2(5)
H(1W3)	377(4)	397(3)	796(3)	4.6(6)
H(2W3)^a	104	390	876	5.2

^{a}Not included in the refinement.

Results and discussion

Molecular geometry

The molecule consists of a phenyl ring fused to pyrazole ring with a tetrazole ring connected equatorially to the pyrazole ring. Except for the N(7) nitro-group oxygen atoms, the molecule is planar, with all the nonhydrogen atoms lying within 0.051(2) Å of the mean plane through the molecule (Table 4). The dihedral angle between the mean planes of the phenyl ring and the pyrazole is 1.5°, while the tetrazole ring makes dihedral angles of 2.1° and 3.5°, respectively, with the mean planes of pyrazole and phenyl rings. The N(8) nitro group makes an angle of 0.95°, while the N(7) nitro group makes an angle of 7.6°, with the mean plane of the phenyl ring. The torsion angles C(3)–C(4)–N(7)–O(1) = 7.7(3)° and C(5)–C(4)–N(7)–O(2) = 5.5(3)° are due to the slight twist of the N(7) nitro group.

The bond lengths and angles for the molecule are shown in Fig. 2. The bond length and angles in the phenyl ring have an average value of 1.391(3) Å and 120.0(2)°, respectively. The bond length C(5)–C(6) = 1.411(3) Å is longer, while C(4)–C(5) = 1.361(3) Å is shorter, than the rest of the bond lengths. The bond angles C(3)–C(4)–C(5) and C(5)–C(6)–C(1), at the apices to which the nitro groups are attached, are 122.2(2) and 123.8(2)°, respectively. The enlarged C–C–C angle at C attached to nitro groups is a common feature in nitrofluorenes and in other nitroaromatic compounds (Carter *et al.*, 1966; Iwasaki and Kawano, 1977; Sake Gowda *et al.*, 1982). The C–N(nitro) bond distances have an average value of 1.465(3) Å, and the N–O distances vary between 1.215(3) and 1.222(3) Å. These values agree with those observed in *p*-nitroperoxybenzoic acid (Kim *et al.*, 1970), 2,4-dinitrobenzaldehyde-1*H*-

Table 4. Least-squares plane[a]

Plane: All non-H atoms except nitro groups
$-0.9166X + 0.2288Y - 0.3297Z = 4.8942$

C(1), 0.025(2); C(2), 0.030(2); C(3), 0.010(2);
C(4), −0.033(2); C(5), −0.047(2); C(6), −0.005(2);
C(7), 0.022(2); C(8), 0.008(2); N(1), 0.039(2);
N(2), −0.001(2); N(3), −0.037(2); N(4), −0.048(2);
N(5), 0.021(2); N(6), 0.015(2); N(7),* −0.051(2);
N(8),* −0.006(2); O(1),* 0.117(2); O(2),* −0.180(2);
O(3),* −0.032(2); O(4),* −0.000(2).

[a]The equation of the form $AX + BY + CZ = D$ is shown, along with the deviations from the plane (Å) and the esd's in parentheses; *x*, *y*, and *z* are orthogonal. The asterisk denotes atoms not included in the plane.
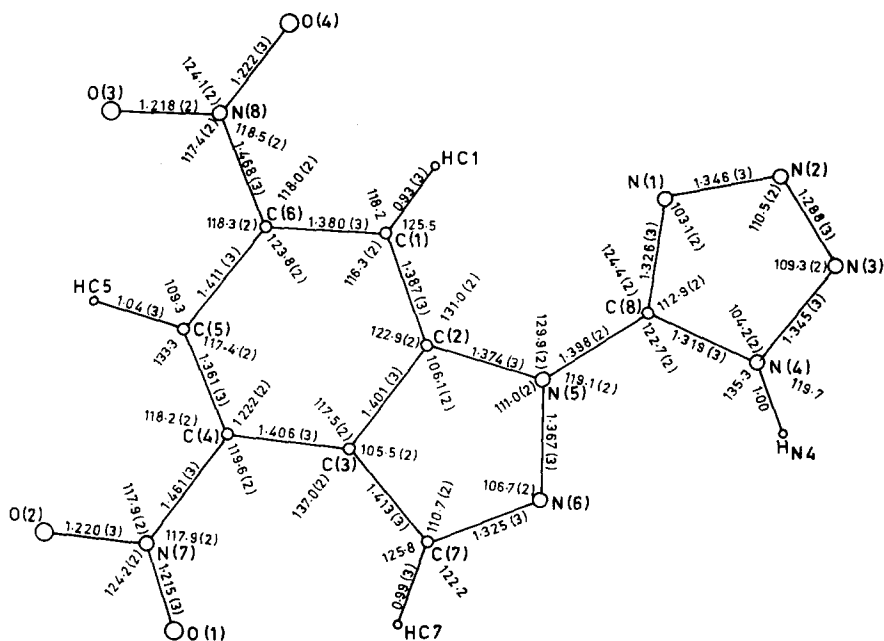
Fig. 2. Bond lengths and angles in the molecule.

tetrazol-5-yl-hydrazone (Sake Gowda *et al.*, 1982), and 1,3,5-trinitrobenzene (Choi and Abel, 1972). The bond lengths and angles associated with the nitro groups suggest the absence of π-electron delocalization from the aromatic ring to nitro groups, whereas the structural features of nitro groups in 3,5-diamino-2,4,6-trinitrophenol (Bhattacharjee and Ammon, 1981) show trends that would be expected for π-electron delocalization.

The bond lengths and angles in the pyrazole ring agree with those observed in the structure of 8-chloro-2-[2-(diethylammonio)ethyl]-2*H*-[1]benzothiopyrano-[4,3,2-*cd*]indazole-5-methanol-monomethane sulfonate (Wei, 1981). The bond lengths in the ring C(7)=N(6) [1.325(3) Å], N(6)–N(5) [1.367 (3) Å], and N(5)–C(2) [1.374(3) Å] have approximate bond orders (Burke-Laing and Laing, 1976) of 1.65, 1.20, and 1.38, respectively, indicating electron delocalization along C(7)=N(6)–N(5)–C(2).

The observed bond lengths in the tetrazole ring compare well with those reported in several structures (Duke, 1971; Britts and Karle, 1967; Sake Gowda *et al.*, 1982). In these compounds, the C(8)–N(1) and C(8)–N(4) bond distances are within 2 esd's of each other, while N(1)–N(2), N(2)–N(3), and N(3)–N(4) are all significantly different. The expected value for a N–N bond is approximately 1.44 Å, and for a N=N bond, approximately 1.24 Å (Kennard

et al., 1972). The bond N(2)–N(3) = 1.288(3) Å exhibits a double-bond character, while the two N–N bonds have partial double-bond character. Using the criteria of Burke-Laing and Laing (1976), the sum of the bond orders over the three N–N bonds is nearly 4. Evidently, there is electron delocalization along these bonds. As the sum of the bond orders over the C(8)–N(1) and C(8)–N(4) bonds is approximately 3, there is electron delocalization along these bonds also.

Molecular packing and hydrogen bonding

The structure consists of planar molecules arranged in layers nearly perpendicular to *a** (Fig. 3). The molecules are linked by a three-dimensional
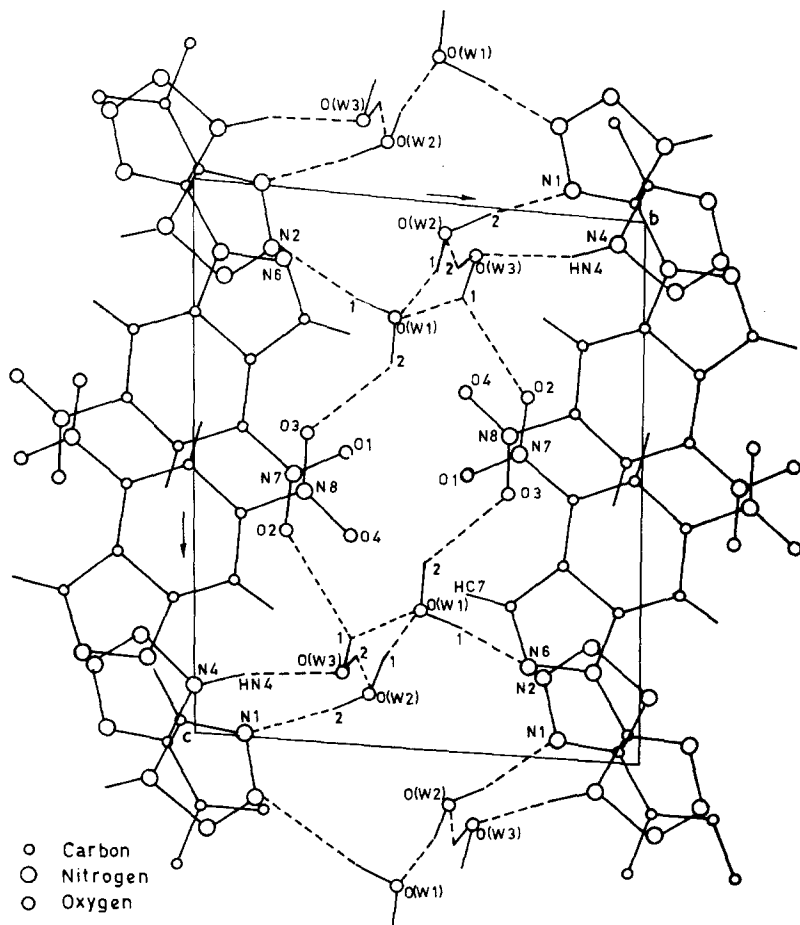

Fig. 3. Molecular packing viewed along *a** axis.

Table 5. Hydrogen bonding parameters in the molecule[a]

Hydrogen bond	$X-H$ (Å)	$H \cdots Y$ (Å)	$X \cdots Y$ (Å)	$X-H \cdots Y$ (deg)
$O(W2)-H(2W2) \cdots N(1)^{iii}$	0.98(3)	1.92(3)	2.891(3)	173(2)
$O(W1)-H(1W1) \cdots N(2)^{ii}$	0.97(3)	1.85(4)	2.821(3)	179(2)
$N(4)-H(N4) \cdots O(W3)^{iv}$	1.00	1.92	2.878(3)	160
$O(W3)-H(1W3) \cdots O(2)^{v}$	1.09(3)	2.24(3)	2.933(3)	120(3)
$O(W1)-H(2W1) \cdots O(3)^{i}$	1.01(4)	2.08(4)	2.885(3)	135(3)
$O(W2)-H(1W2) \cdots O(W1)^{i}$	1.01(5)	1.78(5)	2.774(3)	167(2)
$O(W3)-H(1W3) \cdots O(W1)^{vi}$	1.09(3)	2.03(3)	2.904(3)	135(3)
$O(W3)-H(2W3) \cdots O(W2)^{iii}$	1.08	1.90	2.949(3)	163

[a]Symmetry code: (i) x, y, z; (ii) $1 + x, y, -1 + z$; (iii) $x, 1 + y, 1 + z$; (iv) $x, y, 2 + z$; (v) $1 + x, y, 1 + z$; (vi) $1 + x, 1 + y, 1 + z$.

network of O–H $\cdots$ O, O–H $\cdots$ N, and N–H $\cdots$ O hydrogen bonds; there are several bifurcated hydrogen bonds (Table 5). In addition, there are two nonbonded short contacts between O(W3) and O(W2) at $(x, y, 1 + z)$ and O(W3) and N(6) at $(x, y, 2 + z)$: 2.846(3) and 3.064(3) Å, respectively. The three water molecules are hydrogen bonding to one another and, interestingly, to the oxygen atoms of the nitro groups.

Acknowledgment

References

Bhattacharjee, S. K., and Ammon, H. L. (1981) *Acta Cryst.* B **37**, 2082.
Britts, K., and Karle, I. L. (1967) *Acta Cryst.* **22**, 308.
Burke-Laing, M., and Laing, M. (1976) *Acta Cryst.* B **32**, 3216.
Carter, O. L., McPhail, A. T., and Sim, G. A. (1966) *J. Chem. Soc.* (A) 822.
Choi, C. S., and Abel, J. E. (1972) *Acta. Cryst.* B **28**, 193.
Cromer, D. T., and Mann, J. B. (1968) *Acta Cryst.* A **24**, 321.
Duke, J. R. C. (1971) *J. Chem. Soc. Chem. Commun.* **1**, 2.
Iwasaki, F., and Kawano, Y. (1977) *Acta Cryst.* B **33**, 2455.
Kim, H. S., Chu, S., and Jeffrey, G. A. (1970) *Acta Cryst.* B **27**, 896.
Kennard, O., Watson, D. G., Allen, F. H., Isaacs, N. W., Motherwell, W. D. S., Pettersen, R. C., and Town, W. G. (1972) *Molecular Structures and Dimensions*, Vol. A1 (Oosthoek, Utretcht).

Main, P., Hull, S. E., Lessinger, L., Germain, G., Declercq, J. P., and Woolfson, M. M. (1978) MULTAN-78. A system of computer programs for the automatic solution of crystal structures from X-ray diffraction data (University of York, England, and Louvain, Belgium).

Om Reddy, G., Krishna Mohan, V., Mohan Murali, B. K., and Chatterjee, A. K. (1981) *Thermochim. Acta.* **43**, 61.

Sake Gowda, D. S., Rudman, R., and Ravindra Acharya, K. (1982) *Acta Cryst.* B **38**, 2487.

Sheldrick, G. M. (1976) SHELX-76 program (University of Cambridge, Cambridge, England).

Stewart, R. F., Davidson, E. R., and Simpson, W. T. (1965) *J. Chem. Phys.* **42**, 3175.

Wei, C. H. (1981) *Acta Cryst.* B **37**, 844.