

References

- ABRAHAMS, S. C. & KEVE, E. T. (1971). *Acta Cryst.* **A27**, 157–165.
- APREDA, M. C., FOCES-FOCES, C., CANO, F. H. & GARCÍA-BLANCO, S. (1980). *Acta Cryst.* **B36**, 865–869.
- CANO, F. H., FOCES-FOCES, C. & GARCÍA-BLANCO, S. (1977). *Tetrahedron*, **33**, 797–802.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J. P. & WOOLFSON, M. M. (1978). *MULTAN 78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. of York, England, and Louvain, Belgium.
- STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). The XRAY 70 system. Computer Science Center, Univ. of Maryland, College Park, Maryland.
- WINKLER, F. K. & DUNITZ, J. D. (1971). *J. Mol. Biol.* **59**, 169–182.

Acta Cryst. (1982). **B38**, 2838–2841

Structure of Bis(5-propylphenazinium)–Tris[2,2'-(2,5-cyclohexadiene-1,4-diylidene)bis(propanedinitrile)], (NPP)₂(TCNQ)₃

BY R. HARMS, H. J. KELLER, D. NÖTHE AND D. WEHE

Anorganisch-Chemisches Institut der Universität, Im Neuenheimer Feld 270, D-6900 Heidelberg 1, Federal Republic of Germany

(Received 4 February 1982; accepted 17 May 1982)

Abstract

The title compound, (C₁₅H₁₅N₂)₂(C₁₂H₄N₄)₃, (NPP)₂(TCNQ)₃, $M_r = 1059.18$, $d_c = 1.44 \text{ Mg m}^{-3}$, crystallizes in the triclinic space group $P\bar{1}$ with $a = 8.913(2)$, $b = 12.187(4)$, $c = 13.262(4) \text{ \AA}$, $\alpha = 96.21(2)$, $\beta = 108.13(2)$, $\gamma = 97.36(2)^\circ$, $V = 1340.90 \text{ \AA}^3$ and $Z = 1$. All the molecules are planar with the exception of one TCNQ molecule, in which the planes through the =C(CN)₂ groups are slightly inclined with respect to the ring plane. Mixed stacks of NPP dimers and TCNQ trimers occur along the [011] direction. Final refinement yielded $R = 0.099$ and $R_w = 0.068$ for 1351 reflections. The EPR spectra consist of orientation-dependent structured triplet exciton lines.

Introduction

Phenazine, 5-alkylphenazinium salts and the 5-mono- or 5,10-dialkylated, 5,10-dihydrophenazines as donors form a wide variety of charge-transfer solids with the acceptor 2,2'-(2,5-cyclohexadiene-1,4-diylidene)bis(propanedinitrile)(7,7,8,8-tetracyano-*p*-quinodimethane, TCNQ). They differ in stoichiometry and/or in the molecular arrangement of the donors and the acceptors in the crystal lattice. With 1:1 composition typical *DADA* mixed stacks [as in phenazine (*P*)–TCNQ (Goldberg & Shmueli, 1973*a*), 5,10-dihydro-5,10-dimethylphenazine (Me₂P)–TCNQ (Goldberg & Shmueli, 1973*b*), Me₂P–TCNQF₄ (Soos, Keller,

Ludolf, Queckbörner, Wehe & Flandrois, 1981) and in 5-ethylphenazine(NEP)–TCNQ with σ -bonded and 'chain-linking' (TCNQ)₂²⁻ units (Morosin, Plastas, Coleman & Stewart, 1978; Harms, Keller, Nöthe, Werner, Gundel, Sixl, Soos & Metzger, 1981)], and π -overlapping dimerized structures with *DDAA* columns [as in 5-(1-butyl)phenazinium–TCNQF₄ (Metzger, Heimer, Gundel, Sixl, Harms, Keller, Nöthe & Wehe, 1982)] occur. Segregated regular stacks [as in the famous 5-methylphenazine (NMP)–TCNQ (Fritchie, 1966; Kobayashi, 1975) or in the phenazine-doped NEP–TCNQ, Me₂P–TCNQ and 5,10-dihydro-5,10-diethylphenazine (Et₂P)–TCNQ species (Sandman, 1978; Endres, Keller, Moroni & Wehe, 1980; Dietz, Endres, Keller, Moroni & Wehe, 1982)] can be found in 1:1 salts, too.

Only a few solids deviating from a 1:1 composition have been reported (Sanz & Daly, 1975; Dietz, Endres, Keller & Moroni, 1981; Harms, 1980), one of them [(NMP)₂(TCNQ)₃] with a complicated 2:3 lattice (Sanz & Daly, 1975). The latter compound is unique in this series, so far. Herein we report the preparation, X-ray and EPR data of (NPP)₂(TCNQ)₃, a compound with a lattice very similar to that of (NMP)₂(TCNQ)₃ but with surprising triplet exciton spectra.

Experimental

Chemical preparation

Crystals of (NPP)₂(TCNQ)₃ were grown by mixing hot solutions of (NPP)ClO₄ (100 mg) in absolute

acetonitrile (100 ml) and Li(TCNQ) (65 mg) in absolute 2-propanol (20 ml) and slow cooling of this mixture to 243 K. After several days, a fraction of dark-blue, prismatic crystals with well developed faces was collected together with smaller, black crystals of inferior quality. Only the dark-blue crystals were used for X-ray investigations.

(NPP)ClO₄ was obtained by action of *n*-propyl 2,4-dinitrobenzenesulfonate on phenazine (Harms, 1980) and repeated recrystallization of the resulting dinitrobenzenesulfonate from an ethanol solution containing an excess of LiClO₄, yielding yellow needles, m.p. (dec.) 511–512 K (corr.). Li(TCNQ) was prepared as described earlier (Melby, Harder, Hertler, Mahler, Benson & Mochel, 1962).

X-ray investigations

Rotation and Weissenberg photographs showed that the crystal is triclinic. Unit-cell dimensions (see *Abstract*) were determined from an orientation matrix, derived from the setting angles of 19 independent reflections, centered on a Syntex R3 diffractometer (Mo K α , θ - 2θ scan, $2\theta_{\max} = 45^\circ$, scan range = 1.8°). Data collection was carried out on the diffractometer and an empirical absorption correction was applied to the data. Reflections with $I < 0.5\sigma(I)$ were suppressed. The structure was solved in the space group *P1* by direct methods. The *E* map showed 30 of the non-hydrogen atoms. Three Fourier calculations yielded all of the C and N atoms. A four-cycle refinement with isotropic temperature factors gave $R = 0.187$. After shifting the origin of the unit cell to place one TCNQ on a center of symmetry, the structure was refined in the space group *P* $\bar{1}$ to $R = 0.181$. H atoms were placed in calculated positions and a last five-cycle refinement with weighted functions [weighting scheme: $w = 1/\sigma^2(F)$] yielded final residuals of $R = 0.099$ and $R_w = 0.068$ for 1351 reflections with $I > 0.5\sigma(I)$. The intensity data were only of moderate quality because of the habit of the crystal. The molecular arrangement is of greater interest than the intramolecular parameters.*

All calculations were carried out with the *SHELXTL* program system on a Nova 3 computer (Sheldrick, 1979). Plots were drawn with the *ORTEP* program (Johnson, 1965).

EPR spectra

The EPR data were obtained on a Bruker 418 spectrometer equipped with a Bruker NMR Gaussmeter and an EIP 351 D microwave frequency counter.

* Lists of structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36971 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Results and discussion

Structure description

Atomic coordinates and temperature factors are listed in Table 1. Bond distances and angles are shown in Table 2 according to the numbering scheme of Figs. 2 and 3. H atoms have bond distances between 0.82 (9) and 1.18 (8) Å. The planes through atoms 22 to 26 and through atoms 33 to 37 are slightly twisted with respect to the plane through atoms 24, 35, and 27 to 32 (ring plane), by 3 (1)°. The other ions are planar. The structure consists of mixed stacks of NPP dimers and TCNQ trimers (Fig. 1) along [011] with interplanar distances of 3.13 (2) Å (in the TCNQ trimers) and 3.49 (2) Å (in the NPP dimers). The molecular planes of the NPP and TCNQ ions form an angle of 5 (1)°. The distance between the planes of adjacent donor and acceptor ions is 3.5 (1) Å. A projection of the unit cell onto the *bc* plane is shown in Fig. 1. Only half of each of the two NPP dimers is drawn. The other halves, completing the dimers, are produced by doubling each NPP unit through reflection at the centers of symmetry at (0,0,0) and (0,1,1) respectively. The structure is very similar to that of (NMP)₂(TCNQ)₃ (Sanz & Daly, 1975). The 'ring-bond' overlap of the TCNQ within the trimers (Fig. 2) and the overlap of the NPP dimers (Fig. 3) are rather similar. The interplanar distances are also very similar. Remarkable is the distance between TCNQ's (3.13 Å). This is typical for a strong

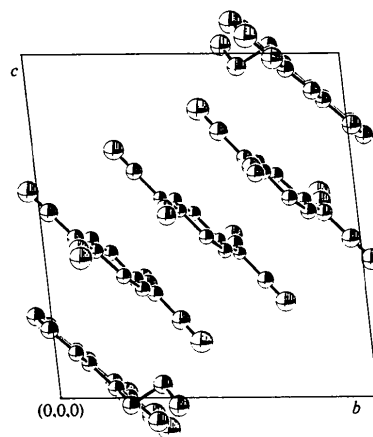


Fig. 1. Projection of the unit cell onto the *bc* plane.

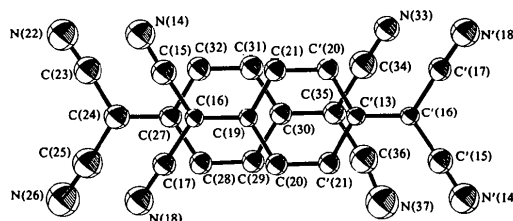


Fig. 2. Projection of two adjacent TCNQ units perpendicular to the ring plane ('ring-bond' overlap) and numbering scheme of acceptors.

Table 1. Atomic coordinates ($\times 10^4$, for H $\times 10^3$) and isotropic temperature factors ($\text{\AA}^2 \times 10^3$)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
C(1)	9381 (12)	-218 (8)	1959 (8)	57 (4)
C(2)	10802 (14)	-403 (9)	2571 (9)	52 (4)
C(3)	12213 (12)	157 (8)	2497 (8)	48 (3)
C(4)	12265 (12)	911 (8)	1806 (8)	39 (3)
C(5)	10752 (11)	1114 (8)	1174 (8)	36 (3)
C(14)	9267 (12)	569 (8)	1212 (8)	41 (3)
N(6)	10635 (10)	1848 (6)	423 (6)	40 (3)
C(7)	9165 (12)	2078 (8)	-169 (8)	40 (3)
C(8)	9055 (14)	2877 (9)	-896 (9)	63 (4)
C(9)	7497 (16)	3002 (10)	-1461 (10)	83 (5)
C(10)	6160 (14)	2417 (10)	-1353 (10)	84 (4)
C(11)	6237 (11)	1661 (10)	-689 (10)	75 (4)
C(12)	7802 (12)	1468 (8)	-18 (8)	45 (3)
N(13)	7838 (10)	721 (7)	621 (7)	49 (3)
C(38)	12145 (12)	2447 (8)	257 (8)	50 (3)
C(39)	12716 (12)	3589 (8)	985 (8)	57 (3)
C(40)	14096 (15)	4185 (9)	660 (10)	68 (4)
N(14)	7947 (11)	7196 (8)	2340 (8)	63 (3)
C(15)	7719 (12)	6602 (8)	2917 (8)	44 (3)
C(16)	7485 (10)	5856 (7)	3632 (7)	26 (3)
C(17)	5829 (13)	5549 (8)	3552 (8)	37 (3)
N(18)	4506 (10)	5357 (7)	3503 (7)	58 (3)
C(19)	8731 (11)	5407 (7)	4300 (7)	26 (3)
C(20)	8418 (11)	4652 (7)	4987 (7)	34 (3)
C(21)	10332 (12)	5744 (8)	4335 (8)	34 (3)
N(22)	9257 (12)	4581 (8)	1522 (8)	78 (4)
C(23)	9066 (13)	3955 (9)	2064 (9)	55 (3)
C(24)	8789 (11)	3200 (8)	2766 (8)	38 (3)
C(25)	7116 (12)	2820 (8)	2669 (8)	52 (3)
N(26)	5831 (11)	2561 (7)	2580 (7)	46 (3)
C(27)	10051 (11)	2799 (8)	3470 (8)	35 (3)
C(28)	9780 (11)	2046 (8)	4163 (8)	39 (3)
C(29)	11022 (11)	1646 (8)	4838 (8)	39 (3)
C(30)	12660 (11)	1954 (7)	4860 (7)	34 (3)
C(31)	12933 (11)	2770 (7)	4196 (7)	37 (3)
C(32)	11689 (11)	3176 (7)	3545 (7)	35 (3)
N(33)	16838 (11)	1949 (7)	5582 (7)	79 (3)
C(34)	15528 (13)	1762 (8)	5539 (9)	64 (4)
C(35)	13901 (12)	1503 (8)	5517 (8)	45 (3)
C(36)	13613 (12)	720 (8)	6191 (8)	53 (3)
N(37)	13467 (11)	121 (7)	6768 (7)	69 (3)
H(1)	818 (9)	-71 (6)	196 (6)	
H(2)	1098 (10)	-95 (7)	312 (7)	
H(3)	1313 (9)	-6 (6)	304 (6)	
H(4)	1349 (9)	147 (6)	188 (6)	
H(8)	992 (9)	321 (6)	-99 (6)	
H(9)	772 (10)	361 (6)	-169 (6)	
H(10)	526 (10)	255 (7)	-178 (6)	
H(11)	544 (10)	137 (6)	-37 (6)	
H(38a)	1179 (9)	239 (6)	-55 (7)	
H(38b)	1295 (10)	185 (6)	28 (6)	
H(39a)	1177 (9)	405 (6)	85 (6)	
H(39b)	1316 (9)	336 (6)	173 (6)	
H(40a)	1452 (10)	490 (7)	116 (7)	
H(40b)	1367 (11)	450 (7)	8 (7)	
H(40c)	1500 (10)	358 (6)	54 (6)	
H(19)	730 (10)	444 (6)	496 (6)	
H(21)	1060 (12)	639 (7)	399 (7)	
H(28)	864 (9)	173 (6)	402 (6)	
H(29)	1081 (10)	126 (6)	526 (6)	
H(31)	1412 (10)	305 (7)	410 (6)	
H(32)	1192 (9)	351 (6)	305 (6)	

Table 2. Interatomic distances (\AA) and angles ($^\circ$)

C(1)-C(2)	1.34 (2)	C(1)-C(14)	1.44 (2)
C(2)-C(3)	1.39 (2)	C(3)-C(4)	1.37 (2)
C(4)-C(5)	1.42 (1)	C(5)-C(14)	1.42 (2)
C(5)-N(6)	1.40 (1)	N(6)-C(7)	1.38 (2)
N(6)-C(38)	1.54 (1)	C(7)-C(8)	1.43 (2)
C(7)-C(12)	1.42 (2)	C(8)-C(9)	1.39 (2)
C(9)-C(10)	1.36 (2)	C(10)-C(11)	1.34 (2)
C(11)-C(12)	1.47 (2)	C(12)-N(13)	1.31 (1)
N(13)-C(14)	1.32 (1)	C(38)-C(39)	1.53 (1)
C(39)-C(40)	1.55 (2)	N(14)-C(15)	1.15 (2)
C(15)-C(16)	1.43 (1)	C(16)-C(17)	1.44 (2)
C(16)-C(19)	1.40 (1)	C(17)-N(18)	1.15 (1)
C(19)-C(20)	1.42 (1)	C(19)-C(21)	1.42 (1)
C(20)-C'(21)	1.38 (1)	N(22)-C(23)	1.14 (2)
C(23)-C(24)	1.43 (2)	C(24)-C(25)	1.47 (2)
C(24)-C(27)	1.40 (1)	C(25)-N(26)	1.11 (2)
C(27)-C(28)	1.42 (2)	C(27)-C(32)	1.44 (1)
C(28)-C(29)	1.37 (1)	C(29)-C(30)	1.45 (1)
C(30)-C(31)	1.44 (1)	C(30)-C(35)	1.39 (1)
C(31)-C(32)	1.36 (1)	N(33)-C(34)	1.14 (2)
C(34)-C(35)	1.43 (2)	C(35)-C(36)	1.43 (2)
C(36)-N(37)	1.14 (2)		
C(2)-C(1)-C(14)	121 (1)	C(1)-C(2)-C(3)	121 (1)
C(2)-C(3)-C(4)	123.8 (9)	C(3)-C(4)-C(5)	115 (1)
C(4)-C(5)-N(6)	120.8 (9)	C(4)-C(5)-N(14)	123.9 (9)
N(6)-C(5)-C(14)	115.3 (8)	C(5)-N(6)-C(7)	121.0 (9)
C(5)-N(6)-C(38)	120.7 (8)	C(7)-N(6)-C(38)	118.2 (8)
N(6)-C(7)-C(8)	121 (1)	N(6)-C(7)-C(12)	115.9 (9)
C(7)-C(8)-C(9)	123.1 (9)	C(7)-C(8)-C(9)	115 (1)
C(8)-C(9)-C(10)	124 (1)	C(9)-C(10)-C(11)	122 (1)
C(10)-C(11)-C(12)	120 (1)	C(7)-C(12)-C(11)	116 (1)
C(7)-C(12)-N(13)	125.4 (9)	C(11)-C(12)-N(13)	118 (1)
C(12)-N(13)-C(14)	116.6 (9)	C(1)-C(14)-C(5)	115.5 (1)
C(1)-C(14)-N(13)	119 (1)	C(5)-C(14)-N(13)	126 (1)
N(6)-C(38)-C(39)	109.6 (9)	C(38)-C(39)-C(40)	105.7 (9)
N(14)-C(15)-C(16)	178 (1)	C(15)-C(16)-C(17)	113.6 (8)
C(15)-C(16)-C(19)	123.2 (9)	C(17)-C(16)-C(19)	123.1 (9)
C(16)-C(17)-N(18)	177 (1)	N(18)-C(17)-C(20)	120.6 (9)
C(16)-C(19)-C(21)	120.0 (9)	C(20)-C(19)-C(21)	119.3 (8)
C(19)-C(20)-C'(21)	119.5 (9)	C(19)-C(21)-C'(20)	121.2 (9)
N(22)-C(23)-C(24)	178 (1)	C(23)-C(24)-C(25)	116.7 (9)
C(23)-C(24)-C(27)	122 (1)	C(25)-C(24)-C(27)	122 (1)
C(24)-C(25)-N(26)	178 (1)	C(24)-C(27)-C(28)	121.7 (9)
C(24)-C(27)-C(32)	120.8 (9)	C(28)-C(27)-C(32)	117.5 (8)
C(27)-C(28)-C(29)	121.1 (9)	C(28)-C(29)-C(30)	121.8 (9)
C(29)-C(30)-C(31)	116.5 (8)	C(29)-C(30)-C(35)	121.1 (9)
C(31)-C(30)-C(35)	122.4 (9)	C(30)-C(31)-C(32)	121.0 (9)
C(27)-C(32)-C(31)	121.9 (9)	N(33)-C(34)-C(35)	178 (1)
C(30)-C(35)-C(34)	123 (1)	C(30)-C(35)-C(36)	122 (1)
C(34)-C(35)-C(36)	115.7 (9)	C(35)-C(36)-N(37)	176 (1)

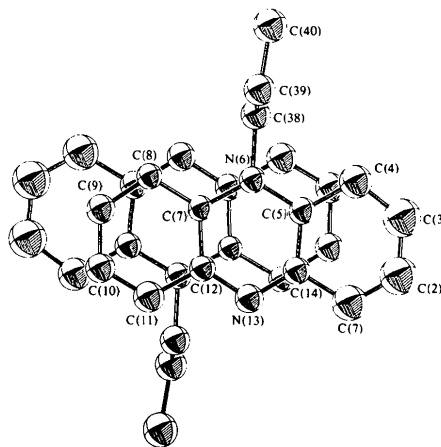


Fig. 3. Projection of two adjacent NPP units perpendicular to the ring plane and numbering scheme of the donor.

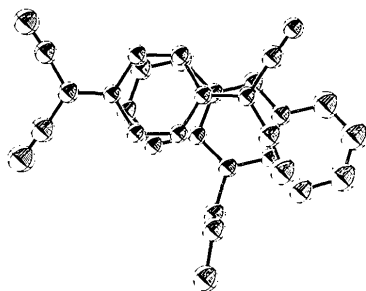


Fig. 4. Projection of a NPP unit onto an adjacent TCNQ acceptor

interaction as in many TCNQ salts. On the other hand the distance of 3.49 Å between NPP's corresponds to a weak interaction, found in weak charge-transfer complexes.

Nevertheless, the 'ring-ring' overlap between NPP and TCNQ's (Fig. 4) differs from that observed in the $(\text{NMP})_2(\text{TCNQ})_3$ complex.

Typical single-crystal EPR spectra are shown in Fig. 5. They have been obtained by rotating the magnetic field in an arbitrary plane containing the Z axis of the zero-field tensor. Besides the $S = \frac{1}{2}$ signal triplet absorptions with a maximum fine-structure line splitting of 295 Gs (1 Gs = 10^{-4} T) can be discerned. The zero-field parameters as derived from single-crystal measurements are $D = 0.0138 \text{ cm}^{-1}$ and $E = 0.0023 \text{ cm}^{-1}$. The intensity $\Delta^2 H \times h$ of the fine-structure lines of width ΔH and peak-to-peak height h is temperature dependent. A logarithmic plot of $\Delta^2 H \times h \times T$ over the reciprocal temperature gives a straight line. According to the well known expression for the susceptibility, χ , of triplet systems, $\chi \times T \sim \exp(-J/kT)$, one obtains for the singlet-triplet separation a value of $J = 0.27 \text{ eV}$ ($1 \text{ eV} = 1.60 \times 10^{-19} \text{ J}$). The zero-field parameters as well as the activation energy J are very similar to those found in $(\text{NEP})_2(\text{TCNQ})_2$ (Harms, Keller, Nöthe, Werner, Gundel, Sixl, Soos & Metzger, 1981). Nevertheless, the crystal structures and even the molecular structures are *very different*. In $(\text{NEP})_2(\text{TCNQ})_2$, for instance, σ -bonded dimers are formed by the TCNQ molecules. Thus it can be stated that similar parameters obtained from EPR do not necessarily point to similar crystal structures even when the constituting molecules are similar. From Fig. 5 it can be seen that except for some special orientations each of the fine-structure lines is additionally split into several lines. The question whether this splitting should be assigned to a partly resolved hyperfine structure or whether electronic states of higher than triplet multiplicity are responsible for this splitting cannot be answered at this time. Further investigations on this problem are in progress.

This work was supported by DFG Ke 135/25 and the structural investigations in part by Stiftung Volkswagenwerk.

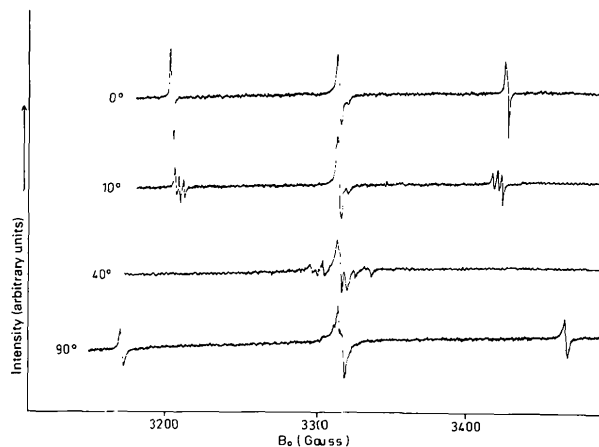


Fig. 5. Room-temperature EPR spectra for different crystal orientations of $(\text{NPP})_2(\text{TCNQ})_3$.

References

- DIETZ, K., ENDRES, H., KELLER, H. J. & MORONI, W. (1981). *Z. Naturforsch. Teil B*, **36**, 952–955.
- DIETZ, K., ENDRES, H., KELLER, H. J., MORONI, W. & WEHE, D. (1982). *Z. Naturforsch. Teil B*. In the press.
- ENDRES, H., KELLER, H. J., MORONI, W. & WEHE, D. (1980). *Acta Cryst.* **B36**, 1435–1440.
- FRITCHIE, C. J. JR (1966). *Acta Cryst.* **20**, 892–898.
- GOLDBERG, I. & SHMUELI, U. (1973a). *Acta Cryst.* **B29**, 440–448.
- GOLDBERG, I. & SHMUELI, U. (1973b). *Acta Cryst.* **B29**, 421–431.
- HARMS, R. H. (1980). Dissertation, Univ. of Heidelberg, Federal Republic of Germany.
- HARMS, R. H., KELLER, H. J., NÖTHE, D., WERNER, M., GUNDEL, D., SIXL, H., SOOS, Z. G. & METZGER, R. M. (1981). *Mol. Cryst. Liq. Cryst.* **65**, 179–196.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- KOBAYASHI, H. (1975). *Bull. Chem. Soc. Jpn*, **48**, 1373–1377.
- MELBY, L. R., HARDER, R. J., HERTLER, W. R., MAHLER, W., BENSON, R. E. & MOCHEL, W. E. (1962). *J. Am. Chem. Soc.* **84**, 3374–3387.
- METZGER, R. M., HEIMER, N. E., GUNDEL, D., SIXL, H., HARMS, R. H., KELLER, H. J., NÖTHE, D. & WEHE, D. (1982). *J. Chem. Phys.* In the press.
- MOROSIN, B., PLASTAS, H. J., COLEMAN, L. B. & STEWART, J. M. (1978). *Acta Cryst.* **B34**, 540–543.
- SANDMAN, D. J. (1978). *J. Am. Chem. Soc.* **100**, 5230–5232.
- SANZ, F. & DALY, J. J. (1975). *J. Chem. Soc. Perkin Trans.* **2**, pp. 1146–1150.
- SHELDRIK, G. M. (1979). *SHELXTL*. An integrated system for solving, refining, and displaying crystal structures from diffraction data. Univ. of Göttingen, Federal Republic of Germany.
- SOOS, Z. G., KELLER, H. J., LUDOLF, K., QUECKBÖRNER, J., WEHE, D. & FLANDROIS, S. (1981). *J. Chem. Phys.* **74**, 5287–5294.