KLYNE, W. & PRELOG, V. (1960). *Experientia*, **16**, 521–523.

MAIN, P., LESSINGER, L., WOOLFSON, M. M., GERMAIN, G. & DECLERCQ, J. P. (1977). *MULTAN 77. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. de York, Angleterre, et Louvain-la-Neuve, Belgique.

ROQUES, R., BELLAN, J., ROSSI, J. C., GERMAIN, G. & DECLERCQ, J. P. (1979). *Acta Cryst.* B**35**, 2467–2470.

STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1972). The XRAY system – version of June 1972. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.

TEXIER, F. & BOURGEOIS, J. (1976). *Bull. Soc. Chim. Fr.* pp. 487–492.

TRUCE, W. E. & BRADY, D. G. (1966). *J. Org. Chem.* **31**, 3543–3550.

ZACHARIAS, D. E. (1970). *Acta Cryst.* B**26**, 1455–1464.

Acta Cryst. (1980). B**36**, 1121–1126

The Neutron Structure at 116 K of the 1:1 Complex of Perdeuterated Parabanic Acid and Urea

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(*Received* 30 *July* 1979; *accepted* 15 *October* 1979)

Abstract

The perdeuterated 1:1 complex of parabanic acid ($C_3D_2N_2O_3$) and urea (CD_4N_2O) at 116 K is monoclinic, space group $P2_1/c$, with $a = 8{\cdot}910\,(3)$, $b = 5{\cdot}597\,(2)$, $c = 14{\cdot}525\,(6)$ Å, $\beta = 108{\cdot}39\,(3)°$, and has four molecules of each kind per unit cell. The nuclear configuration has been determined from 2165 neutron intensities ($\sin\theta/\lambda < 0{\cdot}76$ Å^{-1}, $\lambda = 1{\cdot}0450$ Å) to give e.s.d.'s in apparent bond lengths and angles of 0·001 Å and 0·1°, or less. The configurations of the two molecules are similar to those found in their separate crystal structures, but there are small differences, which appear to be related to the different hydrogen bonding. There is an unusually short hydrogen bond (N···O, 2·66 Å) between parabanic acid N–D and urea O atoms. There are also short C···O distances (2·81, 2·86 Å) between carbonyl groups of different parabanic acid molecules. The polar molecular interactions of parabanic acid are similar to those of the drug-active barbiturates.

Introduction

The structure of the 1:1 crystal complex of parabanic acid and urea (Colman & Medlin, 1970) has been redetermined by neutron diffraction at low temperature as part of a study of the electron charge distribution. Related studies have been carried out for the separate components, parabanic acid (Craven & McMullan, 1979) and urea (Mullen & Hellner, 1978). It is of interest to determine the extent to which a different crystal environment may affect the atomic configuration and charge density in these molecules. We consider parabanic acid to be a simple analog representing the polar ring portion of the barbiturates. As examples of the similarity in the molecular interactions of barbital (5,5-diethylbarbituric acid) and parabanic acid, both form crystal complexes with urea (Gartland & Craven, 1974) and with adenine derivatives (Voet, 1972; Shieh & Voet, 1975). Thus, a detailed knowledge of the molecular and electronic structure of parabanic acid may help in understanding barbiturate drug action.

Experimental

Parabanic acid and urea were deuterated separately by repeated dissolution in 99·8% D_2O and evaporation to dryness. Using 20 ml of D_2O, a solution saturated with respect to both components was formed by warming with an excess of deuterated parabanic acid and urea and allowing to stand at room temperature in a closed container. To the decanted solution, a sample (100 mg) of an equimolar mixture of the deuterated components was added and dissolved by warming. Crystals of the

Table 1. *Crystal lattice parameters*

Parabanic acid–urea complex: $C_3D_2N_2O_3.CD_4N_2O$
Monoclinic; space group $P2_1/c$; $Z = 4$ molecules of each kind/unit cell

	Neutron determinations $\lambda = 1{\cdot}0450\,(2)$ Å				X-ray determination* Mo $K\alpha$, $\lambda = 0{\cdot}7093$ Å
Temperature	116 K	136 K	203 K	233 K	298 K
a	8·910 (3) Å	8·918 (3) Å	8·945 (3) Å	8·969 (5) Å	8·995 (1) Å
b	5·597 (2)	5·591 (2)	5·582 (2)	5·576 (4)	5·573 (1)
c	14·525 (6)	14·561 (5)	14·649 (5)	14·714 (10)	14·798 (2)
β	108·39 (3)°	108·13 (3)°	107·46 (3)°	107·28 (6)°	106·57 (1)°
V	687·4 (5) Å^3	690·0 (5) Å^3	697·7 (5) Å^3	702·7 (8) Å^3	711·0 (2) Å^3

* Ruble, Weber & Craven (1979).

1:1 complex (m.p. 456 K) were grown by slow cooling of this solution. These were monoclinic prisms commonly exhibiting the forms {101}, {10$\bar{1}$}, {001} and {111}. The crystal density of 1·680 (1) Mg m^{-3} at 298 K was measured by flotation in a $CHBr_3/CCl_4$ mixture. The value $r = 0{\cdot}95\,(2)$ was obtained for the D/H isotopic substitution ratio using the X-ray lattice parameters at 298 K and the measured density (Table 1).

The crystal used for neutron data collection weighed 3·08 mg and had a maximum dimension of 4·4 mm along the **b** direction. For subsequent application of neutron absorption and extinction corrections, the crystal was described by eight boundary planes which enclosed a calculated volume of 1·83 mm^3 and gave a mass of 3·07 mg.

The neutron diffraction data were collected with a four-circle diffractometer at the Brookhaven High Flux Beam Reactor, using a neutron beam obtained by (002) reflection from a beryllium monochromating crystal. The neutron wavelength of 1·0450 (2) Å was determined by a least-squares fit of $\sin^2\theta$ data for a standard KBr crystal ($a_0 = 6{\cdot}5966$ Å). The parabanic acid/urea crystal was glued on a hollow aluminum pin fastened within a sealed aluminum can filled with helium gas. The enclosure was cooled by a closed-cycle refrigerator* mounted within the diffractometer χ circle so that the crystal reciprocal-lattice vector [1$\bar{1}$0] was within a few degrees of the φ axis. The lattice parameters (Table 1) were determined by a least-squares fit to $\sin^2\theta$ data for 28 neutron reflections with $41° \leq 2\theta \leq 68°$ which were measured at four temperatures as the crystal was cooled. The crystal temperature was measured by means of a Pt resistor with calibration based on the phase transition of FeF_2 (78·4 K). The neutron intensity data were collected at 116 ± 1 K. A step scan ($\theta/2\theta$) with at least 60 steps was used to obtain integrated intensities for 2574 reflections with $\sin\theta/\lambda \leq 0{\cdot}76$ Å^{-1}. Counts at each step were accumulated during a present monitor count of the direct beam. The scan width was fixed (3·0° in 2θ) for $\sin\theta/\lambda < 0{\cdot}40$ Å^{-1}. Beyond this limit the scan width in 2θ was $(0{\cdot}5 + 4{\cdot}075 \tan\theta)°$. Scans of the neutron scattering from the aluminum pin and cryostat were made over the entire 2θ range at χ values 0, 45 and 90° at φ values which avoided Bragg diffraction from the sample. The features in these scans were broad and it was considered unnecessary to take them into account in estimating backgrounds. Backgrounds were evaluated from the first and last tenth of each scan. The variance in an integrated intensity (I) was assumed to be $\sigma^2(I) = \sigma^2 + (0{\cdot}01I)^2$ where σ^2 is the variance from counting statistics. There were no significant changes in the intensities of five reflections which were measured at intervals of 48 reflections throughout the data collection. The agreement factor for integrated intensities $\sum|\langle I\rangle - I|/\sum\langle I\rangle$ summed over all 409 symmetry-related reflections was 0·02. Of the 2165 reflections not symmetry-related, there were 90 with negative intensities, none of which was significantly different from zero. Using an analytical procedure (de Meulenaer & Tompa, 1965; Templeton & Templeton, 1973), neutron absorption corrections were applied and absorption-weighted mean crystal path lengths were calculated. The linear absorption coefficient ($\mu = 2{\cdot}40$ m^{-1}) was calculated with the assumption that deuteration was complete.

Full-matrix least-squares refinement of structure parameters was carried out with a modified version of the computer program by Busing, Martin & Levy (1962), so as to minimize $\sum w\Delta^2$ where $\Delta = F^2_{\rm obs} - F^2_{\rm calc}$, and $w = 1/\sigma^2(F^2_{\rm obs})$. Neutron coherent scattering lengths were assumed to be 5·80 for O, 6·65 for C, 9·40 for N and 6·67 fm* for D (Koester, 1977). Initially, the atomic positional parameters were taken from Colman & Medlin (1970) and an overall isotropic

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* Air Products and Chemicals, Inc., DISPLEX® Model CS-202.

* The femtometre (1 fm = 10^{-15} m) is not to be confused with the Fermi unit.

Table 2. *Atomic parameters*

All positional parameter values are $\times 10^5$, with e.s.d.'s in parentheses.

(*a*) Parabanic acid

	x	*y*	*z*
N(1)	42475 (6)	−44906 (10)	−39769 (3)
D(1)	49480 (10)	−57829 (16)	−41301 (6)
C(2)	36822 (8)	−25673 (13)	−45845 (5)
O(2)	39233 (10)	−21875 (16)	−53482 (6)
N(3)	27891 (6)	−11567 (9)	−41809 (3)
D(3)	21301 (10)	3107 (16)	−45497 (6)
C(4)	27619 (8)	−20667 (13)	−33171 (5)
O(4)	21256 (10)	−12712 (17)	−27641 (6)
C(5)	37434 (8)	−43856 (13)	−31822 (5)
O(5)	39856 (10)	−57816 (17)	−25214 (6)

(*b*) Urea

	x	*y*	*z*
N(1)	19650 (7)	23278 (11)	−64065 (4)
D(11)	25439 (12)	8002 (19)	−61726 (7)
D(12)	21380 (12)	31472 (19)	−69755 (7)
C	11654 (8)	34040 (13)	−58787 (5)
O	10558 (11)	24831 (18)	−51182 (6)
N(3)	4599 (6)	54990 (11)	−61982 (4)
D(21)	−618 (11)	63621 (17)	−57686 (6)
D(22)	6341 (14)	62949 (19)	−67700 (7)

temperature factor $U = 0·02$ Å^2 was assumed. In the final cycles, the refinement consisted of the nuclear positional and anisotropic thermal parameters, the coherent scattering lengths for individual N and D nuclei, a scale factor and an isotropic extinction parameter, a type I crystal with a Lorentzian distribution of mosaicity being assumed (Becker & Coppens, 1974). The refinement was ended with all parameter changes less than $0·2\sigma$ except for the scale factor $(0·5\sigma)$ and extinction parameter $(1·4\sigma)$. The final agreement factors were $R = (\sum|\Delta|)/\sum F^2_{\rm obs} = 0·037$, $R_w = [(\sum w\Delta^2)/(\sum wF^4_{\rm obs})]^{1/2} = 0·043$ and $[\sum w\Delta^2/(n_{\rm obs} - n_{\rm param})]^{1/2} = 1·61$, where $\Delta = F^2_{\rm obs} - F^2_{\rm calc}$. Final atomic positional parameters are in Table 2.*

Neutron extinction was found to be significant but not severe, with $g = 0·111\,(5) \times 10^4$ rad^{-1}. The reflection 211 was most affected $(0·75F^2_{\rm calc})$ and there were three other reflections with correction factors less than 0·90.

The refined values of the neutron scattering lengths ranged from 9·23 (3) to 9·25 (3) fm for the four N nuclei and from 6·43 (3) to 6·57 (3) fm for the six apparent D nuclei. The latter gave an average value of 6·50 fm with r.m.s. deviation of 0·05. If values 6·67 and −3·74 fm are assumed for the scattering lengths of D and H (Koester, 1977), the observed average scattering length corresponds to $r = 0·984\,(5)$ in the D/H isotopic substitution ratio, which agrees with the value $r = 0·95\,(2)$ from the crystal density. The differences in r at the six nuclear sites are not significant.

Discussion

The neutron low-temperature crystal structure confirms the X-ray structure of Colman & Medlin (1970).* All nuclear distances and angles involving thermal centroids have e.s.d.'s of 0·001 Å and 0·1°. Values involving D atoms and intermolecular distances (Fig. 1, Table 3) are subject to thermal-motion corrections which cannot be reliably estimated, but are likely to be at least 5σ for distances. The bond lengths and angles in Fig. 2(*a*,*b*) have been corrected for rigid-body motion

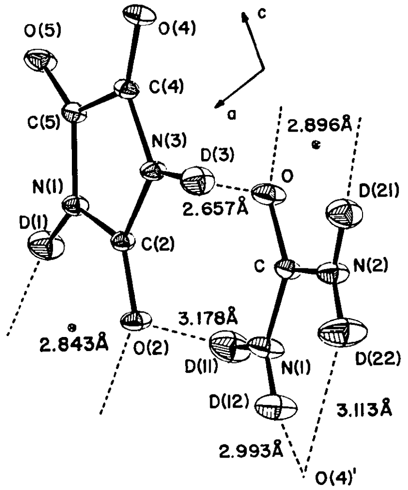

Fig. 1. Atomic nomenclature for parabanic acid (left) and urea (right). Thermal ellipsoids are shown as 50% probability envelopes (Johnson, 1976). These molecules represent the repeating unit in a hydrogen-bonded ribbon, for which D···O interactions and N···O distances are shown.

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* Tables of anisotropic thermal parameters, the rigid-body analyses, least-squares planes of the molecules, and the observed and calculated F^2 values, together with $\sigma(F^2)$, mean path length $(\bar{l})$ and calculated extinction factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34933 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* The cell constants at room temperature given by Colman & Medlin, $a = 9·137\,(14)$, $b = 5·623\,(3)$, $c = 15·013\,(45)$ Å, $\beta = 109°\,8\,(2)'$, are somewhat different from the remeasured X-ray values in Table 1. When our values are used with the atomic positional parameters of Colman & Medlin, bond lengths and angles are in satisfactory agreement with the present neutron values.

Table 3. *Intermolecular distances and angles*

E.s.d.'s are 0·001 Å in distances and less than 0·1° in angles. All values are subject to thermal-motion corrections which cannot be determined, but are likely to be significantly greater than the e.s.d.'s.

(*a*) Hydrogen bonds

	d(N···O)*	*d*(D···O)	∠N–D···O
N(3)–D(3)···O	2·657 Å	1·606 Å	177·5°
N(1)–D(1)···O(2)	2·843	1·832	168·2
N(1)–D(11)···O(2)	3·178	2·194	167·5
N(1)–D(12)···O(4)†	2·993	2·088	149·6
N(2)–D(22)···O(4)	3·113	2·250	144·2
N(2)–D(21)···O	2·896	1·892	171·3

(*b*) Carbonyl–carbonyl interactions‡

	Distance O···C	Angle C–O···C
C(5)–O(5)···C(5)	2·811 Å	133·1°
C(5)–O(5)···C(4)	2·859	114·0

* See Fig. 1.

† N(1)–D(12) forms a weak interaction with O(5) of the same molecule which accepts this hydrogen bond. The corresponding distances and angle are 3·060, 2·432 Å, 108·5°.

‡ See Fig. 3, bottom right.

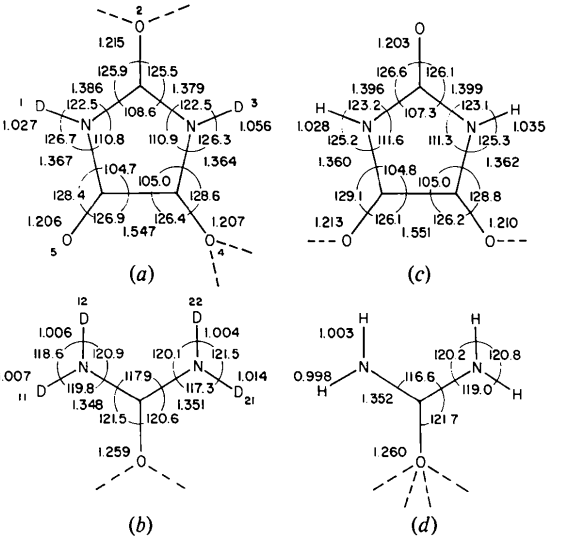

Fig. 2. Bond lengths (Å) and angles (°) with all values corrected assuming rigid-body motion. (*a,b*) Molecules at left show present results (complex at 116 K). (*c*) Parabanic acid at 298 K (Craven & McMullan, 1979). (*d*) Urea at 298 K (Pryor & Sanger, 1970). Dashed lines represent the hydrogen bonds formed at each O atom in these crystal structures.

using the librational tensors.* For parabanic acid, the maximum corrections are 0·005 Å for the C(4)–C(5) length and 0·09° for the C(2)–N(1)–D(1) angle. The atomic thermal parameters for this molecule (Fig. 1) give a good fit to rigid-body behavior (Schomaker & Trueblood, 1968) when the D atoms are omitted. The resulting distance and angle corrections are thus considered to be more reliable than for the urea molecule, where the rigid-body fit is less convincing. This appears to be due to the relatively large thermal motion of the urea D atoms (Fig. 1). The D atoms cannot be omitted from the urea rigid body because the remaining atoms lie on two intersecting lines, thus giving rise to a singularity in the least-squares procedure (Johnson, 1970). Although the resulting librational corrections for urea are large (0·009 Å for C–O), they produce agreement with the librationally corrected values of bond lengths and angles (Fig. 2*d*) in the room-temperature neutron crystal structure of urea itself (Pryor & Sanger, 1970).

In the crystal structures of parabanic acid (Craven & McMullan, 1979) and urea (Pryor & Sanger, 1970) the molecules are planar, but in the crystal complex both are slightly puckered.* In parabanic acid, there is a twist about a molecular axis from C(2) through the midpoint of the C(4)–C(5) bond. However, such puckering does not adequatly account for the 0·144 Å displacement of D(3) from the best molecular plane. It is noted that D(3) forms a very short hydrogen bond with the urea O atom (Fig. 1, Table 3). The D(3) displacement may strengthen this interaction because the arrangement N(3)–D(3)···O is made more nearly linear. All urea D atoms are slightly displaced towards the same side of the molecular plane, giving some pyramidal character to the bonding of the N atoms.

There are small differences in both lengths and angles of the parabanic acid molecule as determined in the urea complex and in its own crystal structure at 298 K (Fig. 2*a,c*). These are greatest in the bonds formed at C(2). In the complex, there is a longer C(2)–O(2) bond (0·012 Å) with conjugated shortening of the C(2)–N bonds (0·010, 0·020 Å) and there is a smaller internal ring angle (1·3°). The differences remain significant when the e.s.d.'s are given doubled values (0·002 Å and 0·2°) because of possible uncertainty in the librational corrections. The substitution of H for D atoms, and the slight difference in molecular conformation may contribute to the distance and angle differences. However, the nature of the molecular hydrogen bonding (as indicated by the dashed lines in Fig. 2) is considered to have a much greater effect. Thus atom O(2) in crystals of parabanic acid forms no hydrogen bonds, whereas in the complex it forms two. Similar correlations between hydrogen bonding and molecular structure have been described for the barbiturates (Craven, Cusatis, Gartland & Vizzini, 1973).

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* See deposition footnote. R.m.s. principal values of the librational tensors are 4·1, 2·2, 1·8° for parabanic acid and 6, 4, 3° for urea.

* See deposition footnote. Distances of non-D atoms from the best least-squares planes are all within 0·02 Å for parabanic acid and 0·005 Å for urea. In parabanic acid, D-atom displacements (x10³ Å) are D(1), 38; D(3), −144, and for urea D(11), 23; D(12), 28; D(21), 41; D(22), 10.

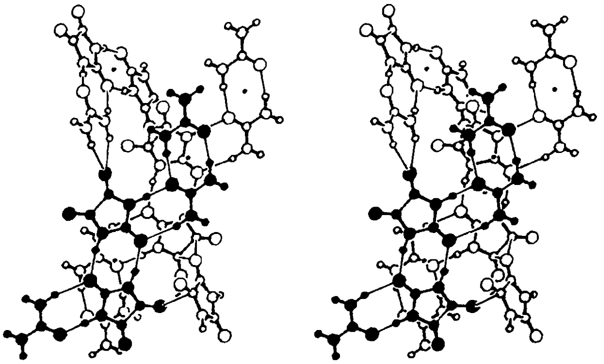

Fig. 3. Stereoview of the structure (Johnson, 1976) projected on the plane of one hydrogen-bonded ribbon (atoms shown solid). Circles of decreasing size represent O, N, C, D atoms. Important molecular interactions (C···O, bottom right; hydrogen bonds) are represented by thinner lines than the covalent bonds. Dots are centers of symmetry.

The structure of the crystal complex (Fig. 3) consists of alternating tilted stacks of nearly planar hydrogen-bonded ribbons which are symmetty related and parallel to the crystal planes (211) and (2$\bar{1}$1). Within ribbons, each molecule forms pairs of ND···O hydrogen bonds with its two neighbors (Figs. 1, 3 and Table 3). The ribbon sequence is $(AABB)_n$ where A and B are urea and parabanic acid. The urea atoms D(12) and D(22) which are *trans* with respect to the urea C—O bond are both hydrogen bonded with the same O(4) atom of parabanic acid (Fig. 1). These urea H atoms form a similar hydrogen-bond arrangement in the crystal structure of urea (Pryor & Sanger, 1970) and in the crystal complex of urea with barbital (Gartland & Craven, 1974). In the parabanic acid complex, these are the only hydrogen bonds between different ribbons (Fig. 3, top left). Atom O(5) of parabanic acid is the only oxygen which is not hydrogen bonded. However, the C(5)—O(5) carbonyl group is directed towards atoms C(5) and C(4) of parabanic acid in a neighboring ribbon (Fig. 3, bottom right), forming short O···C distances (2·811, 2·859 Å; Table 3). Similar short intermolecular distances between carbonyl groups occur in related crystal structures (Voet, 1972; Shieh & Voet, 1975), the shortest (2·77 Å) being in parabanic acid (Craven & McMullan, 1979). The nature of such interactions is not well understood (Bolton, 1964; Bürgi, Dunitz & Shefter, 1974; Craven & McMullan, 1979).

The hydrogen bonds between the two components are of particular interest. The hydrogen bond N(3)—D(3)···O in which parabanic acid is donor and urea is acceptor is unusually short [N···O, 2·66 Å; see Table 6 in Hsu & Craven (1974*a*) and Tables 4 and 6 in Gartland & Craven (1974)], indicating a very strong interaction, whereas the hydrogen bond N(1)D(11)···O(2) in which these roles are reversed is unusually long (N···O, 3·18 Å) and is presumably weak. The remaining ND···O hydrogen bonds between molecules of the same kind are of intermediate character. We suggest that the strong N(3)—D(3)···O hydrogen bond is an important factor for the existence of the crystal complex. While these molecules are both amides having dual hydrogen-bonding donor and acceptor capability, parabanic acid like the barbituric acids appears to be more effective as donor, while urea is more effective as acceptor. These relationships were discussed by Gartland & Craven (1974), and have been found to apply to NH···N as well as NH···O bonds involving barbiturates (Hsu & Craven, 1974*b*; Wang & Craven, 1979).

Much of this work was carried out at Brookhaven National Laboratory under contract with the US Department of Energy. It was supported in part by the Office of Basic Energy Sciences and in part by a grant GM-22548 from the National Institutes of Health. We thank Mr Joseph Henriques for technical assistance. Dr R. Shiono's modification of the *ORTEP* computer program by Dr C. K. Johnson was used in preparing Figs. 1 and 3.

References

BECKER, P. J. & COPPENS, P. (1974). *Acta Cryst.* A**30**, 129–147.

BOLTON, W. (1964). *Nature* (*London*), **201**, 987–989.

BÜRGI, H. B., DUNITZ, J. D. & SHEFTER, E. (1974). *Acta Cryst.* B**30**, 1517–1527.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.

COLMAN, P. M. & MEDLIN, E. H. (1970). *Acta Cryst.* B**26**, 1547–1553.

CRAVEN, B. M., CUSATIS, C., GARTLAND, G. L. & VIZZINI, E. A. (1973). *J. Mol. Struct.* **16**, 331–342.

CRAVEN, B. M. & McMULLAN, R. K. (1979). *Acta Cryst.* B**35**, 934–945.

GARTLAND, G. L. & CRAVEN, B. M. (1974). *Acta Cryst.* B**30**, 980–987.

HSU, I-N. & CRAVEN, B. M. (1974*a*). *Acta Cryst.* B**30**, 974–979.

HSU, I-N. & CRAVEN, B. M. (1974*b*). *Acta Cryst.* B**30**, 988–993.

JOHNSON, C. K. (1970). *Crystallographic Computing*, edited by F. R. AHMED, p. 214. Copenhagen: Munksgaard.

JOHNSON, C. K. (1976). *ORTEP* II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.

KOESTER, L. (1977). *Neutron Physics*, edited by G. HOHLER, p. 1. Berlin: Springer.

MEULENAER, J. DE & TOMPA, H. (1965). *Acta Cryst.* **19**, 1014–1018.

MULLEN, D. & HELLNER, E. (1978). *Acta Cryst.* B**34**, 1624–1627.

PRYOR, A. W. & SANGER, P. L. (1970). *Acta Cryst.* A**26**, 543–558.

RUBLE, J. R., WEBER, H. P. & CRAVEN, B. M. (1979). Unpublished work.

SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* B**24**, 63–76.

SHIEH, H. S. & VOET, D. (1975). *Acta Cryst.* B**31**, 2192–2201.

TEMPLETON, L. K. & TEMPLETON, D. H. (1973). Abstr. Am. Crystallogr. Assoc. Meeting, Storrs, Connecticut, p. 143.

VOET, D. (1972). *J. Am. Chem. Soc.* **94**, 8213–8222.

WANG, A. & CRAVEN, B. M. (1979). *J. Pharm. Sci.* **68**, 361–363.

Acta Cryst. (1980). B**36**, 1126–1130

Structure of Thermochromic Schiff Bases. II. Structures of *N*-Salicylidene-3-aminopyridine and *N*-(5-Methoxysalicylidene)-3-aminopyridine

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(*Received* 5 *November* 1979; *accepted* 17 *December* 1979)

Abstract

The structures of the weakly thermochromic compounds *N*-salicylidene-3-aminopyridine (I) and *N*-(5-methoxysalicylidene)-3-aminopyridine (II) were determined by X-ray crystallographic methods. The crystal structure of (II) is disordered, the molecules having two orientations of the pyridine ring in a statistical sense. Bond distances and the packing arrangement of (I) are similar to those of *N*-salicylidene-2-aminopyridines, but the pyridine ring is tilted by 14·8° with respect to the rest of the molecule. [Crystal data: (I) $C_{12}H_{10}N_2O$, space group $P2_1/n$, a = 15·233 (8), b = 4·692 (2), c = 14·316 (7) Å, β = 98·19 (4)°, Z = 4; (II) $C_{13}H_{12}N_2O_2$, space group $P2_1/n$, a = 4·649 (2), b = 20·288 (11), c = 12·068 (5) Å, β = 97·04 (3)°, Z = 4.]

Introduction

In a previous study (Moustakali-Mavridis, Hadjoudis & Mavridis, 1978) we determined the crystal structures of the Schiff base *N*-salicylidene-2-aminopyridine and three of its derivatives. All four molecules are planar in the crystalline state, stacked along the shortest axis with similar interplanar distances (~3·45 Å), and exhibit strong thermochromic behaviour, in agreement with an earlier proposed classification (Bregman, Leiserowitz & Ozaki, 1964, and references therein). In this classification, planar geometry is associated with thermochromism, non-planar with photochromism.

Assuming that the phenomenon of thermochromism and/or photochromism is a monotonic function of the molecular geometry, *i.e.* of the angle variable which defines the orientation of one ring with respect to the other, we are exploring whether certain geometries can be allotted on the basis of their response towards heat or light. *N*-Salicylidene-3-aminopyridine (I) and *N*-(5-methoxysalicylidene)-3-aminopyridine (II) exhibit only weak thermochromism in the crystalline state. Their structure analyses were undertaken to shed more light on the relation between geometry in the crystalline state and chromo behaviour.

Experimental

The title compounds were synthesized by known methods (Vogel, 1966). Single crystals were obtained by cooling solutions in cyclohexane. Suitable crystals 0·7 × 0·25 × 0·15 mm mounted along the longest axis were used for data collection. The diffraction conditions determined by photographic and diffractometric methods ($h0l$: $h + l = 2n$; $0k0$: $k = 2n$) and the monoclinic symmetry indicate the space group $P2_1/n$ for both compounds. The densities were measured by flotation in silver nitrate solution.

0567-7408/80/051126-05$01.00