

orthorhombique à faces centrées. Ces écarts sont tous nettement supérieurs aux écart-types correspondants et les plus grands écarts se produisent suivant l'axe c' , direction d'allongement du cristal. Les atomes d'azote se répartissent en deux groupes. Le premier groupe d'atomes [N(1) à N(6)] constitue un réseau pseudo-cubique à faces centrées. Leur association avec les ions UO_2F_5^- est analogue à celle du chlorure de sodium. Le deuxième groupe [N(1') à N(6')] et leurs homologues qui s'en déduisent par symétrie détermine un réseau pseudo-cubique simple de paramètre moitié du réseau cubique à faces centrées décrit précédemment. La coordinence des ions ammonium est élevée mais difficile à estimer en raison des imprécisions sur les distances calculées au cours de cette détermination de structure. Les ions sont situés dans des cages formées par les atomes de fluor et d'oxygène.

Il est maintenant intéressant de comparer les structures des composés $\text{K}_3\text{UO}_2\text{F}_5$ et $(\text{NH}_4)_3\text{UO}_2\text{F}_5$, signalés par Baker (Baker, 1879) comme étant isomorphes. La structure du pentafluoxyuranate de potassium a été étudiée par Zachariassen (Zachariassen, 1954). La maille quadratique de $\text{K}_3\text{UO}_2\text{F}_5$ et la pseudo-maille orthorhombique de $(\text{NH}_4)_3\text{UO}_2\text{F}_5$ ont des dimensions comparables. L'ion UO_2F_5^- adopte la même configuration de dipyramide pentagonale dans les composés. Les atomes d'uranium et de potassium dans l'un des composés et les atomes d'uranium et d'ammonium dans l'autre se placent aux noeuds de réseaux pseudo-

cubiques tels qu'ils ont été définis précédemment. Une différence notable entre les deux structures est l'orientation relative des dipyramides dans la maille. Alors que dans le pentafluoxyuranate d'ammonium les dipyramides gardent la même orientation à savoir que leur axe reste parallèle à l'axe binaire b (Fig. 6), dans le sel de potassium, à cause de la présence des axes quaternaires, les axes des dipyramides parallèles aux vecteurs de base a ou b de la maille, prennent deux orientations perpendiculaires l'une à l'autre. Une autre différence est l'existence pour le pentafluoxyuranate d'ammonium d'une surstructure liée à de faibles déplacements des atomes d'uranium par rapport aux noeuds du réseau orthorhombique à faces centrées. Nous voyons que les deux sels ne sont pas isostructuraux et par là ne doivent pas être isomorphes.

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The Crystal and Molecular Structure of 2-Dimethylsulfuranylidene malononitrile

BY A. T. CHRISTENSEN* AND W. G. WITMORE†

Syntex Research, Institute of Steroid Chemistry, Palo Alto, California, U.S.A.

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Crystals of $[\text{CH}_3]_2\text{S}^+-\text{C}^-\text{[CN]}_2$ are orthorhombic, space group $Pna2_1$ with four molecules in the unit cell. The cell parameters are $a = 12.768 \text{ \AA}$, $b = 5.691 \text{ \AA}$ and $c = 9.378 \text{ \AA}$, estimated standard deviations of 0.008 \AA . The trial structure was refined by three-dimensional, full-matrix, least-squares procedures. The hydrogen atom positions were obtained from a difference Fourier map. The final R value was 0.048. The mean $\text{S}-\text{CH}_3$ bond distance is 1.82 \AA and the $\text{S}-\text{C[CN]}_2$ bond distance is 1.72 \AA . The $\text{C}-\text{C}$ bond distances are 1.40 \AA and the $\text{C}-\text{N}$ bond distances 1.16 \AA . The configuration around the central carbon atom is planar. The analysis confirms the view that the stabilization of the carbanion is due mainly to overlap of the carbanion electrons with the sulfur $3d$ -orbitals.

Introduction

Recently there has been an increasing interest in the chemistry of sulfonium ylids (Cook & Moffatt, 1968, and references cited therein), but because of lack of information regarding bond distances and bond angles,

no satisfactory description of the bonding in this class of compounds has been produced. It was therefore felt that the structure of 2-dimethylsulfuranylidene malononitrile would be of interest. The compound forms stable crystals with melting point of $99-100^\circ\text{C}$.

Experimental

Crystals of $[\text{CH}_3]_2\text{S}^+-\text{C}^-\text{[CN]}_2$ were kindly supplied to us by Dr John Moffatt. Preliminary precession photo-

* Syntex Postdoctoral Fellow (1966-1967).

† Present address: Picker Nuclear Western Inc., San Francisco, California, U.S.A.

graphs showed that the crystals are orthorhombic. The systematic extinctions, $h0l$ with h odd and $0kl$ with $(k+l)$ odd, are consistent with the space groups $Pnam$ and $Pna2_1$.

The crystal used for the determination of cell parameters and collection of intensity data had dimensions of approximately $0.20 \times 0.15 \times 0.25$ mm. The calculated linear absorption coefficient for copper radiation is 33 cm^{-1} . No correction for absorption was applied.

Cell dimensions were determined on a Picker diffractometer with full circle goniostat, using Cu radiation. The cell parameters and direction cosines of the reciprocal axes relative to the instrument coordinate system were refined by least-squares. The refinement was based on eleven strong reflections in the 2θ range 66° to 111° .

The following results were obtained: $a = 12.768 \text{ \AA}$, $b = 5.691 \text{ \AA}$ and $c = 9.378 \text{ \AA}$, the e.s.d.'s of the order 0.008 \AA . These values give a calculated density of 1.24 g.cm^{-3} for $Z=4$. The density observed by flotation was 1.23 g.cm^{-3} . Intensities were collected using Ni filtered Cu $K\alpha$ radiation and an automated Picker diffractometer with pulse height discriminator. The method used was the 2θ - θ scan. The intensities of a total of 695 reflections in the range $0^\circ < 2\theta < 158^\circ$ were measured; of these, 660 had an intensity greater than three times the standard deviation. The estimated standard deviation for a recorded number of counts was obtained from the expression $S(N) = N^{1/2} + 0.005 N$. No systematic change was detected in two standard reflections which were measured at regular intervals during the course of the data collection, but the initially colorless crystal darkened slowly as it was exposed to radiation.

Determination and refinement of the structure

A sharpened three-dimensional Patterson function revealed the x and y coordinates of the sulfur atom. The trial structure was first assumed to be in space group $Pnam$, with the sulfur atom and the central carbon atom in special positions on the mirror plane. A Fourier synthesis based on the signs due to the S atom showed that the trial structure in $Pnam$ involved a twofold disorder of the CH_3 and CN groups.

Because of the ambiguity in the space groups, the trial structure was refined by four cycles of three-dimensional full matrix least-squares procedures in both space groups. The atoms were given anisotropic temperature factors in the last three cycles. The R index at this stage was $R=0.15$ for the disordered structure in $Pnam$ and $R=0.066$ for the ordered structure in $Pna2_1$. The much smaller R value indicates $Pna2_1$ to be the correct space group. This is also confirmed by the fact that the refinement in this space group leads to a molecular geometry which is more consistent with accepted values. A final three-dimensional difference Fourier synthesis in $Pna2_1$ revealed the positions of the hydrogen atoms, but showed no other significant

maxima or minima. Reflections with $\sin \theta/\lambda < 0.35$ were now included in a least-squares refinement of the hydrogen atom coordinates; the isotropic temperature factors of the hydrogen atoms were kept constant at $B=3.5 \text{ \AA}^2$. The refinement was concluded with three cycles of least squares in which the position parameters and anisotropic temperature factors of all non-hydrogen atoms were included. The shifts in the last cycle were about 10% of the corresponding e.s.d.'s. The Z parameter of the sulfur atom was arbitrarily set to 0.300. The final R is 0.048, excluding the 'unobserved' reflections.

The positional and thermal parameters for the final structure are given in Tables 1 and 2 respectively.

Table 1. Final position parameters

The e.s.d.'s are set off by a comma and are given in units of the least significant digit.

	x	x	z
S(1)	0.1742, 1	0.0836, 4	0.3000
C(2)	0.2951, 6	-0.0458, 15	0.3191, 17
C(3)	0.1236, 10	-0.1390, 20	0.4759, 13
C(4)	0.0915, 7	-0.1607, 18	0.2414, 15
C(5)	0.3820, 7	0.0660, 17	0.2576, 13
N(6)	0.4527, 7	0.1612, 17	0.2070, 16
C(7)	0.3030, 7	-0.2600, 19	0.3890, 13
N(8)	0.3059, 9	-0.4424, 21	0.4448, 14
H(9)	0.031	0.215	0.454
H(10)	0.118	-0.007	0.505
H(11)	0.176	0.259	0.521
H(12)	0.097	-0.294	0.328
H(13)	0.036	-0.082	0.239
H(14)	0.112	-0.209	0.119

Since the molecule is noncentrosymmetric, analysis of the rigid-body motion of the molecule was done by the method of Schomaker & Trueblood (1968). The root mean square difference between calculated and observed U_{ij} is 0.0050 \AA^2 , so the rigid body model is not satisfactory. The rigid-body tensors are given in Table 3. The maximum librational amplitude is about 5.9° . Observed and calculated structure factors are given in Table 4.

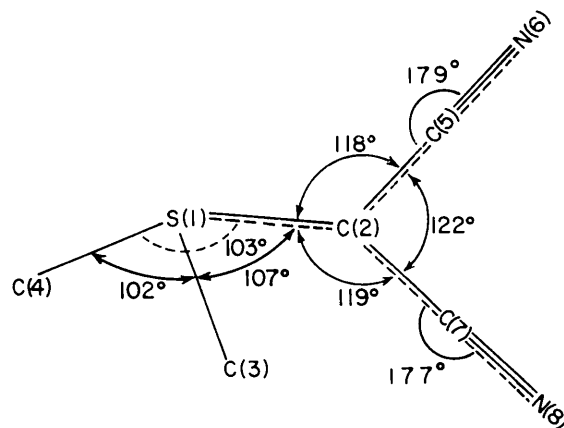


Fig. 1. Bond angles in the molecule.

Computing procedures

The least-squares routine for cell dimensions and diffractometer coordinates was written by A. T. Christensen. The diffractometer settings program was a revised version of the program written by C. T. Prewitt (1964). The revision, done by H. Hope, included a change to full circle geometry and an optimized setting sequence for high angle reflections. The Lp program, the least-squares plane and distance angle programs were written by H. Hope.

The structure factors and the $Pna2_1$ Fourier summations were calculated with programs written by P. K. Gantzel & K. N. Trueblood, the Fourier program

originally specified for space group $P2_12_12_1$ was revised by A. T. Christensen to handle $Pna2_1$. The centrosymmetric Fourier calculations were done with programs written by H. Hope & P. K. Gantzel.

The least-squares program was that of Gantzel, Sparks & Trueblood [ACA no. 317] which minimizes $\sum w[|F_o|K - G|F_c|]^2$. The weighting scheme used was $w = 1/\sigma^2(F_o)$. The scattering factors used were those given by Hanson, Herman, Lea & Skillman (1964). The anisotropic temperature factors are of the form $\exp(-h^2B_{11} + k^2B_{22} + l^2B_{33} + hkB_{12} + hlB_{13} + klB_{23})$.

The R index defined by $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ included observed reflections only.

The program for analysis of rigid-body motion was written by K. N. Trueblood.

The structure

The bond distances and angles were corrected for the effect of molecular libration, (Cruickshank, 1961). The molecular dimensions are shown in Figs. 1 and 2. The uncorrected and the corrected bond distances are compared in Table 5.

The C-S ylid bond is of special interest and it should be noted that the correction of this bond is probably exaggerated. Inspection of Table 2 shows that the B_{ij} 's for atoms S(1) and C(2) are about the same, and the unique origin is approximately 0.64 Å from the center of the C-S ylid bond. The method of Leung & Marsh (1958), which is often used when the rigid body model is unsatisfactory, gives negligible correction for this bond.

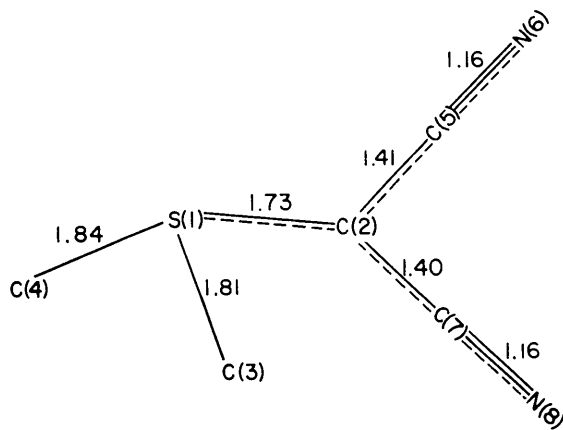


Fig. 2. Bond lengths.

Table 2. *Thermal vibration parameters* $B_{ii} \times 10^4$ and $B_{ij} \times 10^4$

The e.s.d.'s are set off by a comma and are given in units of the least significant digit.

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
S(1)	50, 1	291, 7	124, 3	-7, 5	7, 5	42, 13
C(2)	55, 5	299, 33	150, 18	5, 18	-6, 18	56, 46
C(3)	113, 9	553, 60	162, 17	29, 41	79, 20	-18, 50
C(4)	63, 6	426, 36	207, 18	-53, 25	-47, 18	35, 44
C(5)	54, 5	370, 37	208, 22	3, 24	-13, 15	27, 47
N(6)	60, 6	465, 38	339, 25	-33, 25	42, 21	115, 55
C(7)	78, 7	272, 29	150, 15	14, 25	-19, 18	33, 40
N(8)	131, 10	532, 56	199, 18	-23, 37	-15, 22	157, 52

Table 3. *Results of rigid-body analysis of thermal parameters*

	Eigenvalues	Eigenvectors Direction cosines of the eigenvectors to a , b and c		
Librational tensor, L	35.3 (deg) ²	0.4327	-0.8770	0.2090
	20.4	0.6385	0.1344	-0.7578
	13.3	0.6365	0.4614	0.6181
Translational tensor, T	0.0569 Å ²	-0.4113	0.2125	0.8864
	0.0511	-0.5496	0.7179	-0.4271
	0.0433	-0.7271	-0.6629	-0.1785
Symmetrized screw tensor, S	$\begin{pmatrix} 356 & 276 & 2922 \\ & -576 & 1650 \\ & & 219 \end{pmatrix} \times 10^6 \text{ rad. } \text{Å}$			

The unique origin in fractional coordinates along the crystal axes: 0.24002 0.00425 0.24895.

Table 5. Bond distances and bond angles

	Bond distances		e.s.d.
	Uncorrected	Corrected	
S(1)-C(2)	1.719	1.730	0.008
S(1)-C(3)	1.800	1.810	0.010
S(1)-C(4)	1.831	1.841	0.010
C(2)-C(5)	1.403	1.410	0.014
C(2)-C(7)	1.388	1.395	0.015
C(5)-N(6)	1.155	1.158	0.014
C(7)-N(8)	1.163	1.167	0.016
C(3)-H(9)	1.28		
C(3)-H(10)	0.86		
C(3)-H(11)	1.05		
C(4)-H(12)	1.09		
C(4)-H(13)	0.86		
C(4)-H(14)	1.20		

	Bond angles		e.s.d.
	C(2)-S(1)-C(4)	103.0	
C(2)-S(1)-C(3)	107.3	0.7	
C(3)-S(1)-C(4)	101.7	0.7	
S(1)-C(2)-C(5)	118.3	1.0	
S(1)-C(2)-C(7)	119.3	1.2	
C(5)-C(2)-C(7)	122.1	1.7	
C(2)-C(5)-N(6)	179.0	1.8	
C(2)-C(7)-N(8)	177.2	1.8	

The configuration around the central carbon atom is coplanar within the experimental error. Table 6 gives the least-squares planes calculated. The arrange-

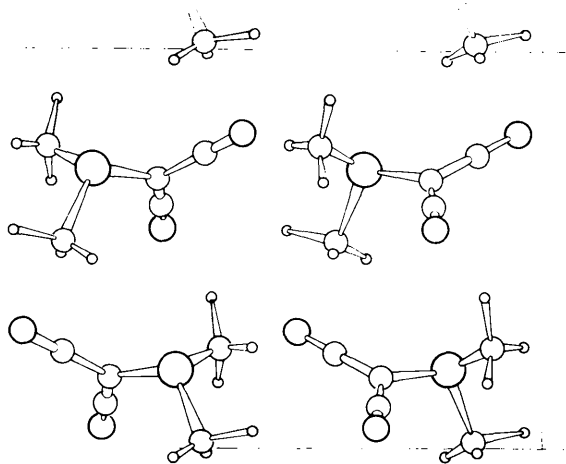


Fig. 3. Projection of the structure along [010]. The unit cell is outlined.

ment around the sulfur atom is, as expected, pyramidal, with the sulfur atom sitting 0.74 Å above the plane through atoms C(2), C(3) and C(4). The torsion angle defined by atoms C(5), C(2), S(1) and C(4) is 131.7° [*i.e.* the angle between the normals to the planes C(5), C(2), S(1) and C(2), S(1), C(4)]. The torsion angle defined by C(7), C(2), S(1) and C(3) is 61.2°.

Comparison of the C-S distance of 1.72 Å with the accepted C-S single bond distance of 1.81 Å and with the $>C=S$ bond lengths found in thiourea (Truter & Kunchur, 1958) and thioacetamide (Truter, 1960) of 1.71 Å and 1.713 Å respectively, leads to the conclusion that there is an appreciable amount of double bond character in the C-S bond of sulfonium ylids.

Truter & Kunchur have discussed the contribution of the ionic resonance forms in the two thioamides, thiourea and thioacetamide, *e.g.* $S=C[NH_2]_2 \rightleftharpoons \bar{S}-C=[NH_2^+]_2 NH_2$. With the completion of the structure determination of thioacetamide, Truter suggests that the structures of the thioamides 'correspond to the purely amide forms' and that 1.71 Å represents the standard bond length for a $C[sp^2]=S$ double bond. More recent structure determinations, however, suggest a shorter 'pure' $C(sp^2)=S$ double bond, *e.g.* 1.66 Å in tetraethylthiuramdisulfide (Karle, Estlin & Britts, 1967) and 1.645 Å in 2,4-dithiouracil (Shefter & Mautner, 1967). It has been suggested that the C-S bonds in the thioamides has only partial double bond character, and that the ionic resonance structures must be considered, a view that is supported by the length of the C(2)-S(1) bond in the sulfonium ylid. The substituent effect on bond lengths may make it difficult, however, to assign a standard 'pure' carbon-sulfur double bond length.

It is of interest to compare the geometry of the sulfonium ylid carbanion with the structure of pyrimidinium dicyanomethylide (Bugg, Desiderato & Sass, 1964, 1965). The authors conclude that the carbanion is nonplanar, thus suggesting a significant localization of charge on the central carbon atom. This is contradicted by molecular orbital calculations. Loftus (1965) finds that the π -electron densities on the central carbon atom of pyrimidinium dicyanomethylide and $C(CN)_3^-$ ion are essentially the same. Enemark & Holm's (1964) calculations on the tricyanomethanide anion show an insignificant net charge on the central carbon atom.

Table 6. Least squares planes

Atom No.	1*	2*	3	4	5*	6	7*	8
Plane to atom distances in Å	-0.004	0.014	1.473	1.314	-0.005	-0.014	-0.005	-0.052
Equation of plane	1.8765X + 2.7932Y + 0.0536Z = 2.9806							
Atom No.	1*	2*	3	4	5*	6*	7*	8*
Plane to atom distances in Å	-0.013	0.023	1.464	-1.318	0.001	-0.010	0.019	-0.020
Equation of plane	1.9557X + 2.7336Y + 8.0989Z = 3.0124							
Atom No.	1	2*	3*	4*	5	6	7	8
Plane to atom distances in Å	-0.737	0.000	0.000	0.000	-0.827	-1.516	1.368	2.5111
Equation of plane	0.3662X - 4.5105Y + 5.7121Z = 2.1372							

* Denotes atoms defining planes.

In their paper on the structure of sodium tricyanomethanide Andersen, Klewe & Thom (1967) conclude that the tricyanomethanide anion exists in a planar trigonal configuration and that the nonplanar configuration around the central carbon atom in pyrimidinium dicyanomethylide is due to packing effects. The mean carbon-carbon distance of 1.40 Å corresponds closely with the value 1.408 Å found in sodium tricyanomethanide. The mean carbon-nitrogen bond length is 1.16 Å.

The double bond character of the C-S ylid bond, and the planarity of the carbanion of the sulfonium ylid confirms the view of Johnson (1966), that the unshared electrons on the ylid carbanion are delocalized into the 3*d*-orbitals of the sulfur atom as well as into the rest of the carbanion. From dipole moment calculations on fluorenylidenedimethylsulfurane, Johnson (1966) predicted a C-S ylid bond of 1.7 Å, a value that corresponds well with the bond length of 1.72 Å found from the X-ray data.

Considering the uncertainty in the van der Waals radius of the hydrogen atoms as well as the uncertainty in their positions, the packing contacts appear to be normal, see Fig. 3.

The authors are indebted to Dr John Moffatt of the Institute of Molecular Biology, Syntex Research for suggesting the problem.

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The Crystal Structure of 1-(2,6-dichlorobenzyl)-6-hydroxy-1,4,5,6-tetrahydronicotinamide Dihydrate

BY HÅKON HOPE

Department of Chemistry, University of California, Davis, California 95616 U.S.A.

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The crystal structure of the 'primary acid modification' product of the DPNH model 1-(2,6-dichlorobenzyl)-1,4-dihydronicotinamide has been determined, identifying the product as 1-(2,6-dichlorobenzyl)-6-hydroxy-1,4,5,6-tetrahydronicotinamide. The compound crystallizes with two molecules of water. The crystals are triclinic plates, cell dimensions: $a = 8.275$, $b = 8.080$, $c = 13.267$ Å (e.s.d. ~ 0.003 Å); $\alpha = 92.17$, $\beta = 101.05$, $\gamma = 116.92^\circ$ (e.s.d. $\sim 0.04^\circ$); space group $P\bar{1}$ with two formula units in the cell. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares methods. The final R is 0.038 for 2044 observed reflections measured with a Picker automatic diffractometer, using Cu $K\alpha$ radiation. With the exception of C(5) and the hydroxy group, the nicotinamide moiety is planar, with the benzyl C(H₂) in the same plane. The amide O is *cis* to the ring double bond, and the hydroxy group occupies a pseudo-axial position. Bond distances were corrected for anisotropic thermal motion effects. The N(1)-C(2) bond distance is 1.356 Å, the other two N-C distances are near 1.47 Å. In the benzene ring the distances are: C(CH₂)-C(Cl), 1.399 Å; C(H)-C(Cl), 1.381 Å; C(H)-C(H), 1.390 Å; C-Cl, 1.748 Å. The internal angle at C(CH₂) is 115.3°; at C(Cl), 123.4° (average). The estimated standard deviations are ~ 0.004 Å for distances and $\sim 0.3^\circ$ for angles.

Introduction

Diphosphopyridine nucleotide participates in a large number of biochemically important red-ox reactions. We can represent its reduced form (DPNH) by formula (1), where R is an adenosine-diphosphate-ribose group.

It has been known for many years (Warburg & Christian, 1934) that DPNH is unstable in acidic solutions, where a reaction known as the 'primary acid modification' will occur. The early studies could only suggest that the reaction took place in the nicotinamide moiety, while no definite conclusions regarding its