

tural data of saturated aliphatic compounds with extensive Cl substitution have suggested paraffinic C—Cl bond lengths for mono- and di-substituted carbon of 1.788 and 1.772 Å, respectively (Bart, Bassi & Calcaterra, 1979). The C—Cl bond distances in (I) differ significantly, namely 1.802 (4) and 1.772 (7) Å on average (range 1.765–1.779 Å) for mono- and di-substituted C atoms, respectively, and confirm the trend for the aforementioned variety of small molecules determined by various techniques, mainly in the gas phase.

The shortest intermolecular distances for C...Cl, C...C, C...H, Cl...Cl, Cl...H and H...H are 3.61, >4.0, 3.87, 3.40, 2.94 and 3.01 Å as compared with the expected van der Waals distances of 3.55, 3.60, 3.00, 3.50, 2.95 and 2.40 Å, respectively. Noteworthy is the absence of C...C, C...H and H...H contacts, indicating that the crystal packing is mainly governed by Cl atoms, as is also clearly visible in the arrangement of the chlorocarbon (I) in the unit cell (Fig. 2).

Thanks are due to Dr P. Massardo for preparation of the sample.

Acta Cryst. (1980). B36, 424–428

Structures of Polyether Complexes.

XI.* A Pseudo-Binuclear Complex Formed by a Linear Oligoether and a Neutral Guest Molecule: Bis[(8-quinolyloxy)ethoxyethyl] Ether–Thiourea

BY G. WEBER AND W. SAENGER†

Abteilung Chemie, Max-Planck-Institut für Experimentelle Medizin, Hermann-Rein-Strasse 3, D-3400 Göttingen, Federal Republic of Germany

(Received 2 July 1979; accepted 9 October 1979)

Abstract

$C_{26}H_{28}N_2O_5 \cdot CH_4N_2S$ is monoclinic, $P2_1/c$, with $a = 13.291$ (3), $b = 13.080$ (4), $c = 16.075$ (5) Å, $\beta = 103.20$ (9)°, $M_r = 524.64$, $Z = 4$, $d_c = 1.281$, m.p. = 415 K, $\mu = 1.389$ mm⁻¹. The thiourea molecule is hydrogen bonded through two N—H—N and one N—H—O(ether) interaction with three of the seven hetero-atoms of the ligand. The remaining four O atoms interact only weakly with the thiourea. The ligand displays an *S*-like configuration with each *S* loop wrapping around one N atom of the thiourea. This is similar to a binuclear linear oligoether complex.

* Part X: Weber & Saenger (1980).

† To whom correspondence should be addressed.

References

- BART, J. C. J., BASSI, I. W. & CALCATERRA, M. (1979). *Acta Cryst.* B35, 2646–2650.
 BENT, H. (1960a). *J. Chem. Phys.* 33, 304–305.
 BENT, H. (1960b). *J. Chem. Phys.* 33, 1259–1260.
 BENT, H. (1960c). *J. Chem. Phys.* 33, 1260–1261.
 CAHN, R. S., INGOLD, C. K. & PRELOG, V. (1956). *Experientia*, 12, 81–94.
 CRUICKSHANK, D. W. J. (1965). In *Computing Methods in Crystallography*, edited by J. S. ROLLETT, Ch. 14. Oxford: Pergamon Press.
 GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A27, 368–376.
 IMMIRZI, A. (1967). *Ric. Sci.* 37, 743–749.
 JOHNSON, C. K. (1965). ORTEP. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
 MOORE, F. H. (1963). *Acta Cryst.* 16, 1169–1175.
 RAZUVAEV, G. A., BOBINOVA, L. M., ZVEZDIN, V. L. & EGORCHKIN, A. N. (1970). *Izv. Akad. Nauk*, 3, 637–640.
 SUTTON, L. E. (1965). *Tables of Interatomic Distances and Configuration in Molecules and Ions*, Spec. Publ. No. 18. London: The Chemical Society.
 VAND, V., EILAND, P. E. & PEPINSKY, R. (1957). *Acta Cryst.* 10, 303–306.

Introduction

The ability of linear polyethers to form stable complexes with alkali- and alkaline-earth-metal cations is well known (Tümmeler, Maass, Weber, Wehner & Vögtle, 1977; Vögtle & Sieger, 1977). With polar neutral guest molecules, however, complexes are mostly observed with cyclic crown ethers (Knoechel, Kopf, Oehler & Rudolph, 1978; Goldberg, 1975).

In a stoichiometric complex of quinol and urea (Mahmoud & Wallwork, 1975), the rather acidic OH groups are involved in hydrogen bridges, but hydrogen bonds to O atoms of linear polyethers have only seldom been reported (Suh & Saenger, 1978).

Since the structure of a complex of the title ligand with RbI has been published previously (Saenger & Brand, 1979) and since the distances Rb⁺...O (2.87

Table 2. Bond distances (Å) of non-hydrogen atoms of the ligand and the thiourea molecule

N(1)—C(2)	1.327 (5)	C(21)—C(22)	1.483 (4)
N(1)—C(9)	1.350 (5)	C(22)—O(23)	1.438 (4)
C(2)—C(3)	1.382 (5)	O(23)—C(24)	1.353 (3)
C(3)—C(4)	1.331 (8)	C(24)—C(25)	1.370 (4)
C(4)—C(10)	1.423 (7)	C(24)—C(32)	1.430 (4)
C(5)—C(6)	1.341 (8)	C(25)—C(26)	1.403 (5)
C(5)—C(10)	1.394 (8)	C(26)—C(27)	1.363 (5)
C(6)—C(7)	1.433 (6)	C(27)—C(33)	1.409 (4)
C(7)—C(8)	1.360 (5)	C(28)—C(29)	1.357 (4)
C(8)—C(9)	1.437 (5)	C(28)—C(33)	1.413 (5)
C(8)—O(11)	1.363 (3)	C(29)—C(30)	1.386 (5)
C(9)—C(10)	1.420 (5)	C(30)—N(31)	1.329 (4)
O(11)—C(12)	1.443 (4)	N(31)—C(32)	1.363 (3)
C(12)—C(13)	1.483 (4)	C(32)—C(33)	1.406 (4)
C(13)—O(14)	1.423 (4)	S(34)—C(35)	1.699 (3)
O(14)—C(15)	1.425 (3)	C(35)—N(36)	1.325 (3)
C(15)—C(16)	1.495 (5)	C(35)—N(37)	1.326 (3)
C(16)—O(17)	1.431 (4)	N(36)—H'(N36)	0.969 (3)
O(17)—C(18)	1.433 (4)	N(36)—H''(N36)	0.917 (3)
C(18)—C(19)	1.493 (5)	N(37)—H'(N37)	0.877 (3)
C(19)—O(20)	1.414 (3)	N(37)—H''(N37)	0.924 (3)
O(20)—C(21)	1.426 (4)		

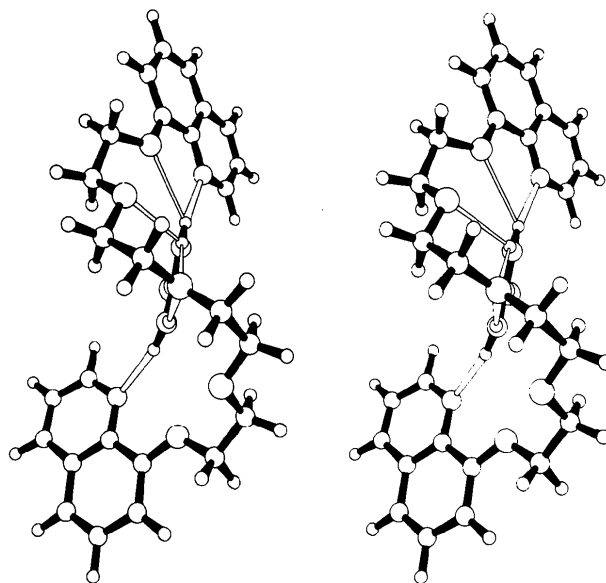


Fig. 2. Stereoscopic view (Johnson, 1965) of the complex.

Table 3. Bond angles (°) of non-hydrogen atoms of the ligand and the thiourea molecule

C(2)—N(1)—C(9)	117.5 (3)	C(21)—C(22)—O(23)	106.7 (2)
N(1)—C(2)—C(3)	123.5 (4)	C(22)—O(23)—C(24)	118.4 (2)
C(2)—C(3)—C(4)	120.0 (4)	O(23)—C(24)—C(25)	125.3 (3)
C(3)—C(4)—C(10)	120.1 (4)	O(23)—C(24)—C(32)	114.4 (2)
C(6)—C(5)—C(10)	123.5 (5)	C(25)—C(24)—C(32)	120.2 (3)
C(5)—C(6)—C(7)	119.1 (4)	C(24)—C(25)—C(26)	119.6 (3)
C(6)—C(7)—C(8)	120.3 (4)	C(25)—C(26)—C(27)	121.8 (3)
C(7)—C(8)—C(9)	120.2 (3)	C(26)—C(27)—C(33)	119.5 (3)
C(7)—C(8)—O(11)	125.4 (3)	C(29)—C(28)—C(33)	119.8 (3)
C(9)—C(8)—O(11)	114.4 (3)	C(28)—C(29)—C(30)	119.2 (3)
N(1)—C(9)—C(10)	118.1 (3)	C(29)—C(30)—N(31)	123.8 (3)
N(1)—C(9)—C(10)	123.0 (3)	C(30)—N(31)—C(32)	117.2 (3)
C(8)—C(9)—C(10)	118.8 (3)	C(24)—C(32)—N(31)	118.2 (3)
C(4)—C(10)—C(5)	126.0 (4)	C(24)—C(32)—C(33)	118.8 (2)
C(4)—C(10)—C(9)	115.8 (4)	N(31)—C(32)—C(33)	123.0 (3)
C(5)—C(10)—C(9)	118.1 (4)	C(27)—C(33)—C(28)	123.2 (3)
C(8)—O(11)—C(12)	118.3 (2)	C(27)—C(33)—C(32)	120.0 (3)
O(11)—C(12)—C(13)	108.7 (2)	C(28)—C(33)—C(32)	116.8 (2)
C(12)—C(13)—O(14)	109.4 (3)	S(34)—C(35)—N(36)	120.8 (2)
C(13)—O(14)—C(15)	110.9 (2)	S(34)—C(35)—N(37)	121.0 (2)
O(14)—C(15)—C(16)	108.3 (3)	N(36)—C(35)—N(37)	118.1 (2)
C(15)—C(16)—O(17)	109.1 (2)	C(35)—N(36)—H'(N36)	124.9 (3)
C(16)—O(17)—C(18)	112.2 (2)	C(35)—N(36)—H''(N36)	119.6 (3)
O(17)—C(18)—C(19)	109.4 (3)	H'(N36)—N(36)—H''(N36)	114.1 (3)
C(18)—C(19)—O(20)	107.7 (3)	C(35)—N(37)—H'(N37)	122.8 (3)
C(19)—O(20)—C(21)	112.4 (2)	C(35)—N(37)—H''(N37)	121.2 (3)
O(20)—C(21)—C(22)	108.0 (2)	H'(N37)—N(37)—H''(N37)	115.9 (3)

trans and O—C—C—O torsion angles are *gauche*. Widened O(23)—C(24)—C(25) and C(22)—O(23)—C(24) bond angles as well as C(7)—C(8)—O(11) and C(8)—O(11)—C(12) may reflect steric repulsion between C(22) and C(25) and between C(7) and C(12).

In the complex of the title ligand with RbI, the host molecule wraps around the cation in a helical manner such that Rb⁺ is coordinated by all the hetero-atoms (Saenger & Brand, 1979). In the present complex the ligand also fits its conformation to the geometry of the guest molecule. Major differences between the Rb⁺ complex and the title compound are: the ligand of the

latter (1) is wrapped in a more elongated configuration because of the larger 'diameter' of the thiourea molecule ($r_{\text{Rb}^+} = 1.47 \text{ \AA}$; 'radius' of thiourea $\approx 1.9 \text{ \AA}$) and (2) adopts an *S*-like configuration as in a binuclear oligoether complex (Weber & Saenger, 1979) because there are *two* NH₂ groups, each of which can accept electrons from the donor atoms.

In the RbI complex of the title ligand (Saenger & Brand, 1979) the five hetero atoms are coplanar and form part of a circle with $r = 2.85 \text{ \AA}$. Rb⁺ deviates by 0.75 \AA from this plane, and thus the mean Rb⁺...hetero-atom distance is 2.95 \AA , *i.e.* slightly longer than the ideal value.

In the present complex each *S* loop can be considered as a semicircle on which hetero-atoms are arranged; the approximate centres of the circles are each occupied by one NH₂ group of thiourea (in order to clarify the pseudo-binuclear character of the present complex both the RbI and thiourea complexes are superimposed in Fig. 3). N(1), O(11), O(14) and O(17) are coplanar within $\pm 0.11 \text{ \AA}$ and lie on a circle with $r = 3.03 \text{ \AA}$. N(37) deviates by 0.9 , H'(N37) by 0.4 and H''(N37) by 0.7 \AA from this plane. The mean N(37)...hetero-atom distance is 3.17 \AA , *i.e.* about 0.2 \AA longer than the respective Rb⁺...hetero-atom distance observed (Saenger & Brand, 1979). The second circle with a mean $r = 2.78 \text{ \AA}$ is formed by hetero-atoms O(17), O(20), O(23) and N(31) which are coplanar within 0.12 \AA . However, N(36) deviates by 1.3 , H'(N36) by 0.9 and H''(N36) by 0.8 \AA from this second plane, and therefore the mean N(36)...hetero-atom distance increases to 3.06 \AA (Rb⁺...hetero-atoms = 2.95 \AA). The dihedral angle between the planes of the circles of the *S* loops is $73 (3)^\circ$.

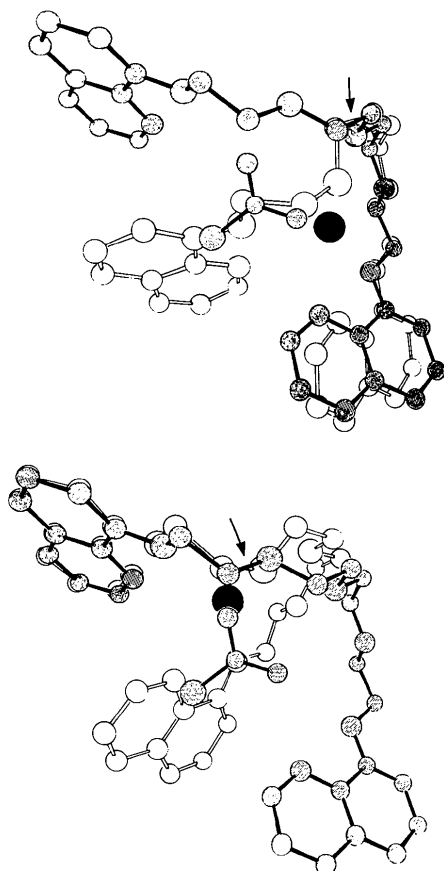


Fig. 3. A comparison of bis[(8-quinolyloxy)ethoxyethyl] etherthiourea (shaded) and the RbI analogue. Molecules are superimposed such that one of the quinoline groups in one molecule overlaps as much as possible with that in the other molecule; Rb⁺ is drawn as a solid sphere. In the upper figure, the quinoline at the right and the attached chains of the two molecules are superimposed. The main deviation occurs at the C—C torsion angle indicated by an arrow which changes from (+) *gauche* in the RbI complex to (–) *gauche* in the thiourea complex. In the lower figure, the other quinolines are superimposed and the deviation occurs at a C—O torsion angle which in the thiourea complex is *trans* but adopts an unusual (+) *gauche* conformation in the RbI complex.

In contrast to a true binuclear oligoether complex (Weber & Saenger, 1979) where the two loops of the *S* are related by twofold crystallographic symmetry, the different radii of both circles of the present complex express the lack of symmetry. This is also indicated by the dihedral angles between the thiourea and the first circle N(1)—O(17), 110 (3)°, and the thiourea and the second circle O(17)—N(31), 118 (3)°.

Hydrogen bonds

According to the sums of the van der Waals radii, distances O···O should be about 2.8, N···O about 2.9, H···N less than 2.7 and H···O less than 2.6 Å in

the hydrogen bridges. From the distances of N(36) to O(17) [3.162 (3) Å], to O(20) [3.292 (3) Å], to O(23) [3.339 (3) Å] and to N(31) [2.995 (3) Å], and of N(37) to N(1) [3.024 (3) Å], to O(11) [3.159 (3) Å], to O(14) [3.168 (3) Å] and to O(17) [3.317 (3) Å] it can be seen that there are few really strong hydrogen-bond bridges. These weak interactions are also indicated by the respective H···N and H···O distances (see Fig. 1).

H-atom parameters determined by X-ray methods are normally of low accuracy. Therefore, the H-atom positions of thiourea were calculated according to the geometry of thiourea obtained from neutron scattering data (Elcombe & Taylor, 1968). However, distances and angles in hydrogen bridges calculated with these 'theoretical' H positions did not differ substantially from those located by Fourier syntheses. Hydrogen bonds exist between H'(N36) and N(31), between H''(N37) and N(1) and probably between H''(N36) and O(17). No interactions are evident for H'(N36)···O(23) and H''(N36)···O(20) (distances >2.6 Å). Very weak interactions might be assumed between H'(N37) and O(17), O(14) and between H''(N37) and O(11), since the distances are approximately equal to the sum of the van der Waals radii. From these distances one might regard H''(N37)···N(1) and H''(N37)···O(11) as well as H'(N37)···O(14) and H'(N37)···O(17), in one *S* loop, as bifurcated hydrogen bonds, whereas in the second *S* loop there are only two 'normal' hydrogen bonds. This also reflects the asymmetry of the complex.

It is noteworthy that there are no interligand hydrogen bonds and that each thiourea molecule complexes with only one ligand molecule. Further, the molecular packing precludes stacking interactions between the quinoline groups.

The authors are grateful to Dr W. Rasshofer and Professor F. Vögtle, University of Bonn, for supplying the sample. Calculations were carried out on the Univac 1108 computer of the Gesellschaft für wissenschaftliche Datenverarbeitung, Göttingen. This work was supported by a grant from the Deutsche Forschungsgemeinschaft.

References

- ELCOMBE, M. M. & TAYLOR, J. C. (1968). *Acta Cryst.* A24, 410–420.
 GOLDBERG, I. (1975). *Acta Cryst.* B31, 754–762.
Handbook of Chemistry and Physics (1974). 54th ed. Cleveland, Ohio: Chemical Rubber Co.
International Tables for X-ray Crystallography (1968). Vol. III. Birmingham: Kynoch Press.
 JOHNSON, C. K. (1965). ORTEP. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
 KNOEHEL, A., KOPF, J., OEHLER, J. & RUDOLPH, G. (1978). *Chem. Commun.* pp. 595–596.
 MAHMOUD, M. M. & WALLWORK, S. C. (1975). *Acta Cryst.* B31, 338–342.

- MAIN, P., LESSINGER, L., WOOLFSON, M. M., GERMAIN, G. & DECLERCQ, J. P. (1977). *MULTAN. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- RASSHOFER, W. & VÖGTLE, F. (1978). *Tetrahedron Lett.* pp. 309–312.
- SAENGER, W. & BRAND, H. (1979). *Acta Cryst.* B35, 838–840.
- SHELDRIK, G. M. (1976). *SHELX*. Program for crystal structure determination. Univ. of Cambridge, England.
- STOUT, G. H. & JENSEN, L. H. (1968). *X-ray Structure Determination*, p. 457. New York: Macmillan.
- SUH, I. H. & SAENGER, W. (1978). *Angew. Chem. Int. Ed. Engl.* 17, 534.
- TÜMLER, B., MAASS, G., WEBER, E., WEHNER, W. & VÖGTLE, F. (1977). *J. Am. Chem. Soc.* 99, 4683–4690.
- VÖGTLE, F. & SIEGER, H. (1977). *Angew. Chem.* 89, 410–412.
- WEBER, G. & SAENGER, W. (1979). *Angew. Chem. Int. Ed. Engl.* 18, 227–228.
- WEBER, G. & SAENGER, W. (1980). *Acta Cryst.* B36, 61–64.

Acta Cryst. (1980). B36, 428–434

The Structures of Two 2-Acyl-1,3-indandiones

BY JAMES D. KORP AND IVAN BERNAL

Chemistry Department, University of Houston, Houston, TX 77004, USA

AND THOMAS L. LEMKE

Department of Medicinal Chemistry, University of Houston, Houston, TX 77004, USA

(Received 19 April 1979; accepted 6 November 1979)

Abstract

Crystals of 2-pivaloyl-1,3-indandione are monoclinic, space group $P2_1/m$, with two molecules positioned on mirror planes in a cell with dimensions $a = 8.411$ (3), $b = 6.897$ (6), $c = 10.522$ (4) Å, $\beta = 105.22$ (3)°; while crystals of 2-acetyl-1,3-indandione are monoclinic, space group $P2_1/n$, with four molecules in a cell of dimensions $a = 5.305$ (3), $b = 7.314$ (2), $c = 23.214$ (10) Å, $\beta = 94.94$ (4)°. Both structures were solved *via* *MULTAN*, and each refined to a conventional R value of 0.038. Both compounds are in the enol form in the solid state, with the enolic H external to the indan system. Considerable steric strain is noted in the pivaloyl derivative due to the bulk of the *tert*-butyl group, and yet this compound is found to have a higher degree of delocalization (stronger internal hydrogen bonding) than the acetyl derivative. NMR and IR spectral analyses, as well as chemical-reactivity studies, support this conclusion derived from the single-crystal X-ray results. The indan portions of both molecules are essentially planar.

Introduction

The reaction of 2-acyl-1,3-indandiones with hydrazine leading to substituted indeno[1,2-*c*]pyrazol-4(1*H*)-ones

has been extensively studied by Mosher & Meier (1970), Mosher, El-Zimaity & Lipp (1971), Mosher & Banks (1971), Mosher, Serridge & Lipp (1972) and Braun & Mosher (1958, 1959). Since the cyclization of β -ketoesters with thiosemicarbazides leads to triazepinones (Losse, Hessler & Barth, 1958) an attempt was made to prepare new and unique tricyclic heterocycles starting from 2-acyl-1,3-indandiones (1). When 2-pivaloyl-1,3-indandione (1a) was treated with thiosemicarbazide in aqueous sodium carbonate, the expected product (2) did not form; instead, 1-hydroxy-4-methylphthalazine (3) was recovered (Lemke & Parker, 1976). However, when the same reaction was attempted with 2-benzoyl-1,3-indandione (1b) or with 2-acetyl-1,3-indandione (1c), none of the *retro*-Claisen condensation product (3) formed. These results suggest important differences in molecular structure for compounds (1a) and (1b,c).

