The Crystal and Molecular Structure of the Cycloadduct from
an Activated Carbodiimide and Methyl Isothiocyanate

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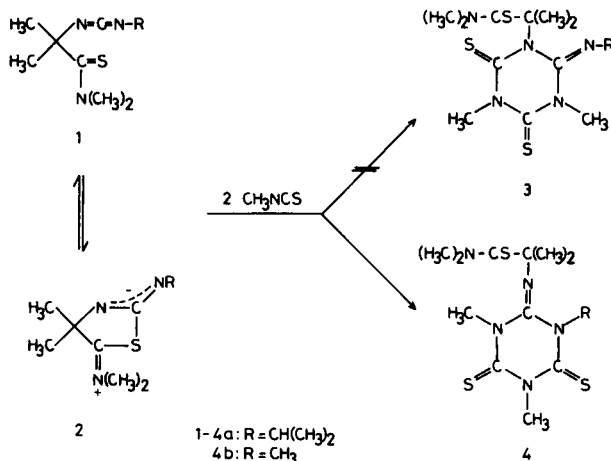Grindelallee 48, 2000 Hamburg 13, Germany

Received February 25, 1977

The crystal and molecular structures of the cycloadduct from isopropyl[α-(dimethylthio-carbamoyl)isopropyl]carbodiimide and methyl isothiocyanate were determined by single-crystal X-ray methods. The product was established to be 2-(1-isopropyl-3,5-dimethyl-4,6-dithioxo-hexahydro-1,3,5-triazine-2-ylidenamino)-N,N-dimethylthioisoburyramide, in which contrary to expectations based on hybridisation the heterocyclic ring adopts a boat conformation.

Introduction.

In contrast to other heterocumulenes such as ketenes and isocyanates, carbodiimides usually show only a limited reactivity in cycloaddition reactions (1). A striking exception is given by carbodiimides **1** having a 2-thiocarb-oxamido substituent (2). Compounds **1** probably exist in an equilibrium with the valencetautomeric dipolar species **2**, which are rendered highly nucleophilic by the negatively charged nitrogen atoms. Thus even a heterocumulene as unreactive as methyl isothiocyanate readily forms a 2:1 adduct with **1a**.

EXPERIMENTAL

The cycloadduct from **1a** and methyl isothiocyanate was prepared as previously described (2). Single crystals were obtained by careful recrystallisation from chloroform/petrol ether.

The compound $C_{14}H_{25}N_5S_3$ was found to crystallise in the triclinic space group P1 with two molecules per unit cell. The following lattice constants were determined (estimated standard deviations of the last digit given in brackets): a = 13.700(4) Å, b = 7.751(3) Å, c = 9.479(4) Å, α = 77.70(6)°, β = 99.16(5)°, γ = 100.11(6)°. Cell volume V = 938.07 Å³. Radiographic density δ_X = 1.273 g/cm³. Linear abosrption coefficient for Mo-K$_\alpha$ radiation μ = 4.72 cm^{-1}.

Intensity data were measured on a Hilger and Watts automatic four-circle diffractometer with Mo-K$_\alpha$ radiation. The determination of the structure was based on 2006 symmetry-independent reflections. The raw data were corrected as usual, neglecting absorption. Eck's programs were used in the correction of the data (3).

Though the number of molecules in the unit cell, statistical tests and the optical inactivity firmly establish the centrosymmetry of the compound under study, the automatic solution of the program MULTAN (4) failed. To get more freedom in the choice of phases it was tried to find the solution by an acentric approach and so the symmetry was reduced to P1. The solution contained two molecules related via a center of symmetry which was not identical with the origin of the unit cell. By a shift of this center of symmetry into the origin the calculation resulted in the real space group P1.

The atomic parameters of all non-hydrogen atoms were refined by least-squares methods utilising anisotropic thermal parameters to give a R value of 0.072 (5). All hydrogen atoms were then located from a difference-Fourier synthesis and included in the calculation. Only the positional parameters of the hydrogen atoms were refined, while the isotropic thermal parameter was fixed at B = 3.0 Å². The refinement converged with a final R value of 0.036. The results of the refinement are compiled in Tables I and II.

Results and Discussion.

The X-ray structural analysis confirms the structure **4a** for the cycloadduct from **1a** and two molecules of methyl isothiocyanate (Figures 1 and 2). Thus the exocyclic nitrogen is the most nucleophilic site in **2**, and both

Concerning the structure of the product, **3a** and **4a** resulting from cycloaddition either with the endocyclic or the exocyclic C-N bond in **2a** seem to be equally probable because of the similar steric requirements of the substituents on both negatively charged nitrogen atoms. Moreover, methyl isothiocyanate may cycloadd not only across the C=N, but also across the C=S bond leading to a variety of possible structures. Though spectroscopic data suggested formula **4a** for the cycloadduct from **1a** and methyl isothiocyanate (2), an X-ray structural analysis seemed desirable for a final solution of the problem.

Table I

Fractional Coordinates and Anisotropic Thermal Parameters (a) of Non-hydrogen Atoms (Standard Deviations in Parentheses)

Atom	X	Y	Z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S1	0.0864(1)	1.3217(1)	-0.5895(1)	0.0074(1)	0.0317(2)	0.0102(1)	0.0079(1)	0.0001(1)	0.0053(1)
S2	0.1183(1)	1.1860(1)	-0.0255(1)	0.0071(1)	0.0201(2)	0.0100(1)	0.0039(1)	0.0033(1)	-0.0021(1)
S3	0.3872(1)	0.6542(1)	0.0976(1)	0.0069(1)	0.0269(2)	0.0105(1)	0.0050(1)	-0.0015(1)	0.0021(1)
N1	0.2352(2)	1.1668(3)	-0.4235(2)	0.0043(1)	0.0149(5)	0.0068(3)	0.0023(2)	0.0013(1)	0.0010(3)
N2	0.0996(1)	1.1700(3)	-0.3082(2)	0.0036(1)	0.0148(5)	0.0090(3)	0.0022(2)	0.0011(2)	-0.0003(3)
N3	0.2468(1)	1.1007(3)	-0.1710(2)	0.0042(1)	0.0129(5)	0.0069(3)	0.0020(2)	0.0004(2)	-0.0016(3)
N4	0.3048(2)	0.9117(3)	-0.3082(2)	0.0037(1)	0.0138(5)	0.0078(3)	0.0020(2)	0.0008(1)	-0.0014(3)
N5	0.2094(2)	0.6848(3)	-0.0466(2)	0.0051(2)	0.0150(5)	0.0091(3)	0.0018(2)	0.0013(2)	0.0004(3)
C1	0.2982(2)	1.2226(4)	-0.5454(3)	0.0057(2)	0.0223(8)	0.0082(4)	0.0028(3)	0.0028(2)	0.0020(5)
C2	0.2812(3)	1.0833(7)	-0.6427(4)	0.0075(3)	0.0445(2)	0.0097(2)	0.0001(5)	0.0023(3)	-0.0080(7)
C3	0.4065(2)	1.2686(6)	-0.4877(4)	0.0060(2)	0.0245(9)	0.0149(5)	-0.0013(4)	0.0046(3)	-0.0040(6)
C4	0.1439(2)	1.2164(3)	-0.4362(3)	0.0047(2)	0.0126(6)	0.0083(4)	0.0020(3)	0.0005(2)	0.0002(4)
C5	-0.0071(2)	1.1848(6)	-0.3176(5)	0.0042(2)	0.0245(9)	0.0151(6)	0.0034(3)	0.0016(3)	-0.0020(6)
C6	0.1567(2)	1.1523(3)	-0.1727(3)	0.0044(2)	0.0093(5)	0.0091(4)	0.0010(2)	0.0017(2)	-0.0000(3)
C7	0.3246(3)	1.1148(5)	-0.0461(3)	0.0059(2)	0.0188(8)	0.0089(4)	0.0033(3)	-0.0010(2)	-0.0042(5)
C8	0.2669(2)	1.0452(3)	-0.2952(2)	0.0032(2)	0.0133(6)	0.0063(3)	0.0006(2)	0.0008(2)	-0.0008(4)
C9	0.3472(2)	0.7650(4)	-0.2020(3)	0.0047(2)	0.0144(6)	0.0090(4)	0.0035(3)	0.0007(2)	-0.0009(4)
C10	0.4600(2)	0.8281(6)	-0.1883(4)	0.0046(2)	0.0249(9)	0.0249(9)	0.0144(5)	0.0014(3)	0.0003(6)
C11	0.3260(3)	0.5966(5)	-0.2755(4)	0.0094(3)	0.0177(8)	0.0134(5)	0.0049(4)	0.0020(3)	-0.0041(5)
C12	0.3073(2)	0.7042(3)	-0.0526(3)	0.0053(2)	0.0116(6)	0.0090(4)	0.0026(3)	0.0005(2)	-0.0006(4)
C13	0.1707(3)	0.6314(6)	0.0944(4)	0.0078(3)	0.0264(9)	0.0119(5)	0.0020(4)	0.0040(3)	0.0003(6)
C14	0.1295(3)	0.6911(6)	-0.1701(4)	0.0043(2)	0.0175(8)	0.0138(5)	0.0015(3)	-0.0002(3)	0.0003(6)

(a) Anisotropic temperature factors are of the form: $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

Table II

Hydrogen Positions
(Standard Deviations in Parentheses)

Atom		X	Y	Z
H11	(C1)	0.439(2)	1.328(4)	-0.570(3)
H21	(C2)	0.302(3)	0.965(5)	-0.588(4)
H22	(C2)	0.214(3)	1.070(5)	-0.674(4)
H23	(C2)	0.320(2)	1.135(4)	-0.724(4)
H31	(C3)	0.365(2)	0.502(5)	-0.219(4)
H32	(C3)	0.415(2)	1.340(5)	-0.414(4)
H33	(C3)	0.437(2)	1.155(5)	-0.442(4)
H51	(C5)	-0.030(2)	1.117(5)	-0.232(4)
H52	(C5)	-0.013(3)	1.308(6)	-0.319(4)
H53	(C5)	-0.038(2)	1.152(4)	-0.409(3)
H71	(C7)	0.329(2)	1.225(5)	-0.019(3)
H72	(C7)	0.305(2)	1.019(5)	0.034(4)
H73	(C7)	0.387(2)	1.106(4)	-0.078(3)
H101	(C10)	0.483(2)	0.866(4)	-0.286(4)
H102	(C10)	0.481(2)	0.933(5)	-0.139(3)
H103	(C10)	0.492(2)	0.726(4)	-0.134(3)
H111	(C11)	0,270(2)	1.326(4)	-0.599(3)
H112	(C11)	0.259(2)	0.554(4)	-0.293(3)
H113	(C11)	0.353(2)	0.626(4)	-0.368(4)
H131	(C13)	0.186(3)	0.503(6)	0.140(4)
H132	(C13)	0.204(2)	0.707(5)	0.156(4)
H133	(C13)	0.101(3)	0.638(5)	0.081(3)
H141	(C14)	0.148(3)	0.741(6)	-0.256(5)
H142	(C14)	0.110(4)	0.585(9)	-0.193(7)
H143	(C14)	0.080(3)	0.737(6)	-0.151(4)
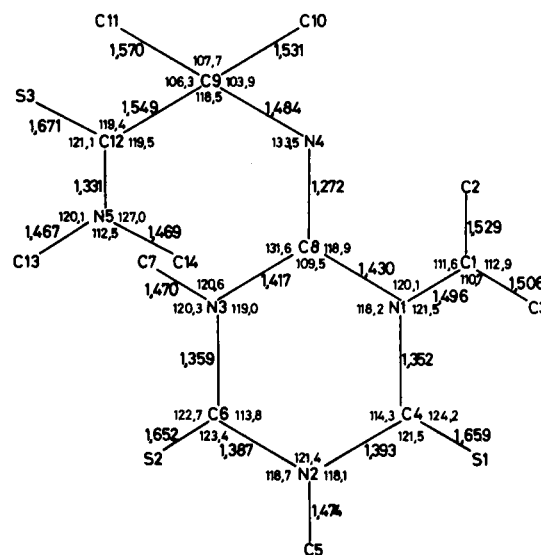
Figure 1. Schematic drawing of the molecule 4a with numbering of atoms, bond distances (Å, maximum standard deviation 0.004 Å) and bond angles (deg., maximum standard deviation 0.3°). Not included are the angles C10-C9-C12 (112.8°) and N4-C9-C11 (107.2°).
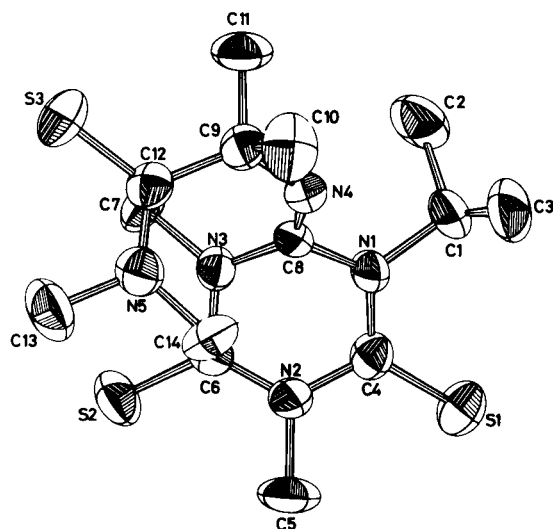
Figure 2. ORTEP drawing of the molecule **4a** showing 50% ellipsoids.

molecules of methyl isothiocyanate react across the CN double bond.

As the N4-C8 double bond carries two different substituents on C8, geometrical isomerism is possible at this site. An inspection of Figure 2 reveals that the molecule adopts the sterically favored E configuration, i.e., a *trans* arrangement of the *N*1-isopropyl group and the *N*4-thiocarboxamido residue. The methine hydrogen at C1 is directed towards the S1 atom; this conformation is known to be preferred in *N*-isopropyl thioamides from nmr spectroscopic studies (6).

The bond lengths in **4a** are mostly within the range expected for the various groups of which the molecule is compiled. As for the dithiobiuret moiety N1-C4(S1)-N2-C6(S2)-N3, when compared with a known dithiobiuret (7), elongations of about 0.05 Å are found only for the terminal C-N bonds (N1-C4, N3-C6). However, these bonds are significantly shorter than the bond lengths N1-C8 and N3-C8, though C8 is, as C4, C6, a formally sp²-hybridised carbon atom. Thus the bond lengths reflect a stronger thiourea-like mesomeric interaction of N1 and N3 with C4-S1 and C6-S2 than is the case within the guanidine system N1-C8(N4)-N3. Here the double bond is essentially localised between C8 and N4 resulting in a CN bond length much shorter than in guanidinium salts (8,9) or in a guanidine with an electron-withdrawing substituent on the C=N nitrogen atom (10). The strongest mesomeric interaction in **4a**, as derived from the distances in the thioamide moiety, is between S3-C12-N5, where no other heteroatom competes with N5 for the electrons of the C12-S3 bond.

In spite of the regular bond lengths and also bond angles found for **4a** (Figure 1), striking deviations from the ex-
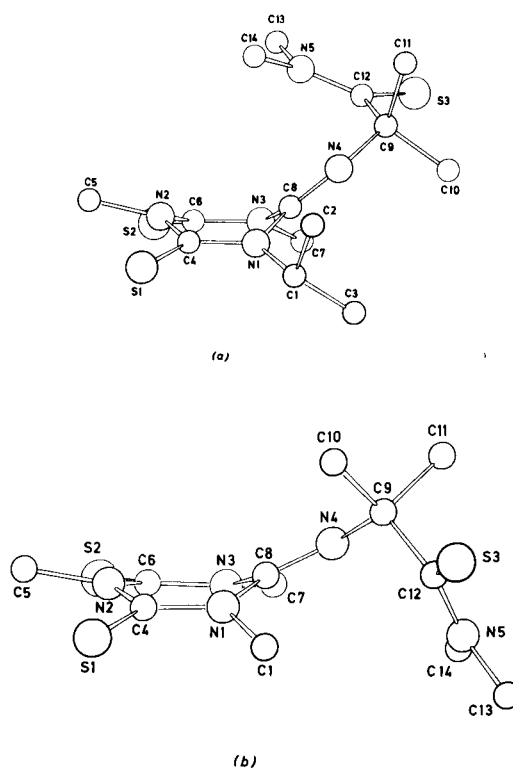

(a)

(b)

Figure 3. ORTEP drawing of **4a** (a) and **4b** (b) in a side elevation of the triazine ring.

pected are observed for the torsional angles in the triazine ring. While the guanidine moiety N1,N3-C8-N4-C9 (maximum deviation 0.02 Å) is planar, other ring atoms deviate from this plane by as much as 1.46 Å (N2) and substituents on ring atoms by about ± 1 Å (C1,S1,S2,C7) and 2.61 Å (C5). Interestingly, the dithiobiuret moiety (vide supra) is strongly bent, giving rise to a boat conformation of the triazine ring (Figure 3a). The angle between the planes C4-N2-C6 and N1-C4-N3-C6 is 25.8°, while the angle of the plane formed by the atoms N1-C8-N3 with the latter plane is 38.9°.

The boat conformation of **4a** contrasts with the results reported for other triazine derivatives with sp²-hybridised ring carbon atoms (11,12) as well as with theoretical considerations based on hybridisation, but allows the bulky side chain on N4 to wind above the ring approximating a helical structure. This results in short intramolecular distances between the strictly planar thioamide group on C9 and ring atoms (C7-C12 3.163, N3-C14 3.296, C7-N5 3.429, C6-C14 3.524 Å), while the shortest intermolecular contact is between S1 and C5 of the next two molecules (4.038 and 4.128 Å). The driving force for the irregular torsional angles seems to be the striving of the molecule to adopt a spherical shape as a whole allowing a close packing in the crystal.

After completion of this work an X-ray study of the similar triazine derivative **4b** was published (13), in which interestingly the ring and the side chain adopt conformations quite different from **4a** (Figure 3b). It appears that the exchange of the methyl group on N1 in **4b** for an isopropyl group as in **4a** forces the side chain on N4 to turn towards the heterocyclic ring with a rotation around the N4-C9 axis combined with a rotation of about 90° around the C9-C12 bond. The steric interactions which the molecule avoids by this change of conformation must be quite strong, for in this conformation the compound **4a** suffers from a more pronounced deformation of the triazine ring than in **4b** and from an increased bending of C7 into a quasi-equatorial position.

Acknowledgments.

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$$R = \frac{\Sigma}{h} \, \| \, F_h^o \, | - | \, F_h^c \, \| \, / \frac{\Sigma}{h} \, | \, F_h^o \, |$$

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