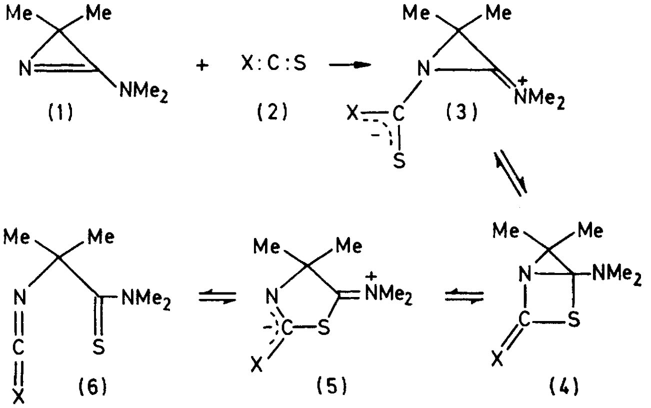
Cycloaddition Reactions of Heterocumulenes. Part 8.[1] Crystal Structure and Valence Tautomerism of 5-Dimethyliminio-4,4-dimethyl-Δ^2-thiazoline-2-thiolate

By **Ernst Schaumann,* Erwin Kausch,** and **Jean-Paul Imbert,** Institut für Organische Chemie und Biochemie, Universität Hamburg, Martin-Luther-King-Platz 6, 2000 Hamburg 13, Germany
Karl-Heinz Klaska and **Rolf Klaska,** Mineralogisch-Petrographisches Institut der Universität Hamburg, Grindelallee 48, 2000 Hamburg 13, Germany

The crystal structure of the title compound has been determined by *X*-ray diffraction. Crystals are monoclinic, space group $P2_1/c$, with $Z = 4$ in a unit cell of dimensions: $a = 7.07_7$, $b = 11.64_4$, $c = 11.95_5$ Å, $\beta = 106.7_4°$. The structure was solved by direct phase-determining methods and refined to R 0.030 for 1 860 reflections. Except for the *C*-methyl groups all non-hydrogen atoms are in a single plane. The positive charge is centred essentially at the N(2) atom and the negative charge at the exocyclic S(2) atom. Solution i.r. measurements and temperature-dependent n.m.r. spectra gave no indication of a dipolar species, but revealed the presence of a 2-isothiocyanatothiocarboxamide, which is formed from the original dipole by ring-opening; this reaction is reversible.

Cycloadditions of 3-dimethylamino-2,2-dimethyl-2*H*-azirine (1) with heterocumulenes proceed *via* dipolar 1 : 1 adducts, which can be isolated for the reaction with isothiocyanates and carbon disulphide.[2,3] The dipolar structure of the isothiocyanate adducts is obvious from i.r. spectroscopic evidence and from the magnetic nonequivalence of the *N*-methyl groups in the ^{1}H n.m.r. spectra observed over a wide temperature range in agreement with the presence of the structural unit $\mathrm{C}\overset{+}{\vdots}\mathrm{NMe_2}$. However, the i.r. and n.m.r. spectra permit no final decision between the dipolar structures (3) and (5).



Scheme 1

(2a)—(6a) X = S
(2b)—(6b) X = N·COPh

Only by *X*-ray structural analysis was it recently possible to assign the formula (5b) to the crystalline product of the reaction between (1) and benzoyl isothiocyanate (2b); also in solution there was no indication of an equilibrium of (5b) with (3b), (4b), or (6b).[4] These observations prompt us to report our studies on the structure of the reaction product from (1) and carbon disulphide (2a).

Experimental

The preparation of the dipolar adduct from (1) and (2a) has been previously described.[2] Single crystals were obtained by careful recrystallization from acetonitrile–diethyl ether. I.r. spectra were recorded on a Perkin-Elmer Spectrophotometer 257, with sodium chloride cells for solution spectra.

X-Ray Structure Analysis.—Intensity data were measured on a Hilger and Watts automatic four-circle diffractometer with Mo-K_α radiation. The raw data were corrected[5] for Lorentz and polarization factors but not for absorption or extinction. The determination of the structure was based on 1 860 symmetry-independent reflections.

Crystal Data.—$C_7H_{12}N_2S_2$, $M = 188$. Monoclinic, $a = 7.07_7$, $b = 11.64_4$, $c = 11.95_5$ Å, $\beta = 106.7_4°$, $Z = 4$, $D_m = 1.32$ g cm^{-3}. Space group $P2_1/c$. Mo-K_α radiation, $\lambda = 0.709\ 26$ Å; μ(Mo-K_α) = 4.72 cm^{-1}.

The phase problem was solved by direct methods[6] by use of the 250 E values with $E \geqslant 1.46$. The program MULTAN led to four sets of phases, of which the one with the highest figure of merit was applied for the calculation of an E map; this showed the maxima of all atoms other than hydrogen. The positions of these atoms were refined by least-squares methods.[7] All hydrogen atoms were then located from a difference-Fourier synthesis. A final least-square calculation with anisotropic thermal parameters for non-hydrogen atoms and isotropic thermal parameters for hydrogen atoms brought the refinement to convergence at R 0.030.

Final atomic positional and thermal parameters are given in Table 1. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21894 (16 pp., 1 microfiche).†

N.m.r. measurements.—Spectra for n.m.r. bandshape analysis were recorded on a JEOL MH 100 spectrometer operating in the frequency sweep mode and utilizing an internal proton lock (tetramethylsilane). The temperature was measured by means of an internal thermocouple connected with a digital voltmeter. A slow sweep rate (0.108 Hz s^{-1}) was used to minimize distortions of the signals.

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† See Notice to Authors No. 7, in *J.C.S. Perkin II*, 1976, Index issue.

[1] Part 7, E. Schaumann and S. Sieveking, *Annalen*, 1976, in the press.

[2] E. Schaumann, E. Kausch, and W. Walter, *Chem. Ber.*, 1974, **107**, 3574.

[3] E. Schaumann, E. Kausch, and W. Walter, *Chem. Ber.*, 1977, in the press.

[4] U. Schmid, H. Heimgartner, H. Schmid, P. Schönholzer, H. Link, and K. Bernauer, *Helv. Chim. Acta*, 1975, **58**, 2222.

[5] J. Eck, unpublished programs.

[6] G. Germain, P. Main, and M. M. Woolfson, *Acta Cryst.*, 1971, **A27**, 368.

[7] W. R. Busing, K. O. Martin, and H. A. Levy, A Fortran LSQ Program, Oak Ridge National Laboratory, Oak Ridge, Tennessee, Report ORNL TM-305, 1962: expanded version of 1971.

TABLE 1

Atomic positional (× 10^4, for H × 10^3) and thermal parameters * (× 10^4 Å^2) with least-square estimated standard deviations in parentheses

Atom	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
S(1)	9 693(1)	6 198(1)	3 995(1)	139	49	62	16	16	−3
S(2)	9 354(1)	4 217(1)	2 363(1)	275(1)	46	79(1)	21(1)	74(1)	−3
C(1)	6 567(3)	8 998(2)	4 368(2)	210(5)	50(2)	74(2)	26(2)	27(2)	−8(2)
C(2)	6 014(2)	6 829(2)	2 817(2)	118(3)	53(2)	59(2)	−5(2)	21(2)	−12(1)
C(3)	9 882(3)	8 259(2)	5 429(2)	179(4)	67(2)	51(2)	−6(2)	8(2)	−9(1)
C(4)	5 402(3)	7 757(3)	1 876(2)	187(5)	75(2)	62(2)	22(2)	5(2)	−3(2)
C(5)	8 231(3)	5 380(2)	2 738(2)	180(4)	43(2)	55(2)	−1(2)	45(2)	−4(1)
C(6)	4 329(3)	6 499(3)	3 338(3)	158(4)	84(2)	104(3)	−29(2)	61(3)	−18(2)
C(7)	7 836(2)	7 175(2)	3 826(2)	120(3)	40(1)	47(1)	−2(2)	26(2)	2(1)
N(1)	6 528(2)	5 801(2)	2 271(2)	162(3)	57(2)	67(2)	−9(2)	29(2)	−18(1)
N(2)	8 023(2)	8 064(2)	4 497(1)	142(3)	42(1)	48(1)	3(1)	20(1)	−1(1)

Hydrogen atom parameters †

	x	y	z		x	y	z
H(11) C(1)	633(4)	911(3)	512(3)	H(41) C(4)	442(4)	743(3)	122(3)
H(12) C(1)	706(4)	968(3)	414(3)	H(42) C(4)	492(4)	840(3)	217(3)
H(13) C(1)	534(4)	878(3)	383(3)	H(43) C(4)	650(4)	796(3)	163(3)
H(31) C(3)	1 057(4)	883(3)	517(3)	H(61) C(6)	388(4)	717(3)	373(3)
H(32) C(3)	966(4)	834(3)	609(3)	H(62) C(6)	325(4)	617(3)	273(3)
H(33) C(3)	1 070(4)	766(3)	551(3)	H(63) C(6)	480(4)	598(3)	395(3)

* Defined by: $T = \exp - (b_{11}h^2 - b_{22}k^2 - b_{33}l^2 - b_{12}hk - b_{13}hl - b_{23}kl)$. † H atom isotropic thermal parameters fixed at 3.0 Å^2.

Two or three spectra were recorded at each of the 23 temperature settings used between 242.7 and 326.7 K.

A simple two-site exchange was assumed, and the theoretical bandshape of the *N*-methyl signals were calculated by use of equations based on McConnell's treatment.[8,9] The τ values were obtained by means of visual fitting of calculated to experimental spectra. The frequency separations $\Delta\nu$ of the coalescing signals were taken directly from the experimental spectra. The signal of the *C*-methyl groups served as internal reference for good resolution and for the calculation of the transversal relaxation time parameter T_2.

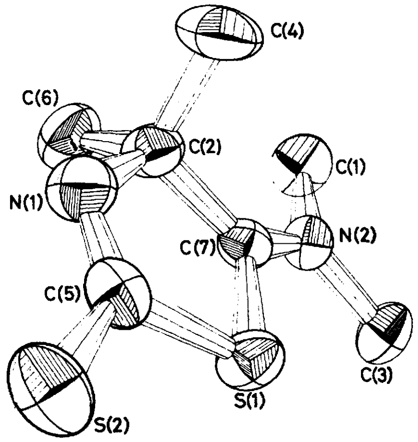

FIGURE 1 Molecular structure of (5a), showing 50% ellipsoids

RESULTS AND DISCUSSION

The *X*-ray structural analysis confirms the structure (5a) for the dipole from (1) and (2a) in the solid state (Figure 1 and Table 2), and not (3a) as we had originally suggested.[2]

All the atoms of the thiazoline ring as well as those of the dimethyliminio-group and the sulphur atom S(2) form a common plane with a maximum deviation of the torsional angle of 5.5° (Table 3); besides the hydrogen atoms, only the methyl carbon atoms C(4) and C(6) are situated below or above this plane. The observed planarity is in accordance with sp^2 hybridization of carbon atoms C(5) and C(7), which are in the centre of the anion and of the cation portion of the molecule, respectively.

TABLE 2

Bond lengths (Å) and angles (°) with least-squares estimated standard deviations in parentheses for non-hydrogen atoms in (5a)

(*a*) Distances

S(1)–C(7)	1.705(2)	C(2)–C(6)	1.545(3)
S(1)–C(5)	1.827(2)	C(2)–C(7)	1.544(3)
S(2)–C(5)	1.695(2)	C(3)–N(2)	1.477(3)
C(1)–N(2)	1.476(3)	C(5)–N(1)	1.272(3)
C(2)–N(1)	1.459(3)	C(7)–N(2)	1.293(3)
C(2)–C(4)	1.530(4)		

(*b*) Angles

C(5)–S(1)–C(7)	90.9(1)	S(1)–C(5)–S(2)	115.9(1)
N(1)–C(2)–C(4)	107.7(2)	N(2)–C(7)–S(2)	127.3(2)
N(1)–C(2)–C(6)	107.3(2)	N(2)–C(7)–S(1)	121.5(1)
N(1)–C(2)–C(7)	107.7(2)	C(2)–C(7)–S(1)	111.1(1)
C(4)–C(2)–C(6)	112.6(2)	C(2)–N(1)–C(5)	116.5(2)
C(4)–C(2)–C(7)	112.7(2)	C(1)–N(2)–C(7)	125.6(2)
C(6)–C(2)–C(7)	108.6(2)	C(3)–N(2)–C(7)	120.1(2)
N(1)–C(5)–S(1)	113.6(2)	C(1)–N(2)–C(3)	114.1(2)
N(1)–C(5)–S(2)	130.5(2)		

TABLE 3

Torsion angles (°) for the non-hydrogen molecular skeleton of (5a)

C(7)–S(1)–C(5)–S(2)	177.6	C(4)–C(2)–N(1)–C(5)	125.2
C(7)–S(1)–C(5)–N(1)	−1.0	C(6)–C(2)–N(1)–C(5)	−112.3
C(5)–S(1)–C(7)–C(2)	2.7	C(7)–C(2)–N(1)–C(5)	3.2
C(5)–S(1)–C(7)–N(2)	−177.9	S(1)–C(5)–N(1)–C(2)	−1.3
C(4)–C(2)–C(7)–S(1)	−122.4	S(2)–C(5)–N(1)–C(2)	180.0
C(4)–C(2)–C(7)–N(2)	58.3	S(1)–C(7)–N(2)–C(1)	175.2
C(6)–C(2)–C(7)–S(1)	111.4	S(1)–C(7)–N(2)–C(3)	0.0
C(6)–C(2)–C(7)–N(2)	−68.0	C(2)–C(7)–N(2)–C(1)	−5.5
N(1)–C(2)–C(7)–S(1)	−3.8	C(2)–C(7)–N(2)–C(3)	180.0
N(1)–C(2)–C(7)–N(2)	176.9		

The C(7)–N(2) distance (1.293 Å) in the cation portion

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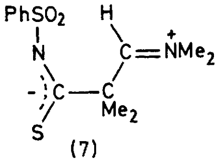
[8] H. M. McConnell, *J. Chem. Phys.*, 1958, **28**, 430.

[9] J.-P. Imbert, Thèse, Université d'Aix-Marseille III, 1975.

[C(1), C(3), N(2), S(1)] is almost the same as found for the iminio-unit of the dipole (7) (1.288 Å).[10] It corresponds essentially to a CN double bond and indicates that most of the positive charge is accumulated at N(2). However, compared with the C(5)–S(1) distance (1.828 Å) the C(7)–S(1) bond length is markedly shorter (1.705 A). This is similar to the situation in (5b)[4] and indicates some contribution of S(1) to the delocalization of the positive charge.


(7)

The anion portion [N(1), C(5), S(2)] of (5a) can be regarded as a thioamide anion. In agreement with an accumulation of negative charge at S(2) the C(5)–N(1) bond (1.272 Å) is shorter and the C(5)–S(2) bond (1.695 Å) longer than is normally found for uncharged thioamides (C–N *ca.* 1.32, C–S *ca.* 1.66 Å).[11] This tendency should also hold for the anion portion of (7), but there it is concealed because of the electron-attracting *N*-sulphonyl residue, which effectively withdraws charge density from the thioamide anion.

Besides mesomeric interactions there is an intermolecular stabilization of the dipolar structure, which is revealed by the arrangement of molecules in the unit cell (Figure 2). The positively charged N(2) atom is situated close to the negatively charged S(2) atom of a neighbouring molecule. The intermolecular distance N(2)–S(2) (3.54 Å) is the shortest intermolecular contact, in agreement with the presence of a significant electrostatic interaction.

In solution, the ^{1}H n.m.r. spectrum of a freshly prepared sample of (5a) shows only a single set of signals. In [^{2}H]chloroform, the *N*-methyl resonance is at 3.43 p.p.m. similar to that for (5b), where a value of 3.63 p.p.m. is reported in agreement with the deshielding effect of a neighbouring positive charge.[4] However, a striking difference between dissolved (5a) and (5b) is revealed in the free-activation enthalpies determined for the two compounds (Table 4). The much lower $\Delta G^‡$ value for the adduct derived from carbon disulphide is not consistent with the formula (5a) for the molecule in solution.

TABLE 4

Free enthalpies of activation $\Delta G^‡$ from coalescence results in [$^2H_6$]dimethyl sulphoxide as well as activation enthalpy $\Delta H^‡$ and activation entropy $\Delta S^‡$ obtained by a total lineshape analysis in [$^2H_6$]acetone

Compound	$\Delta\nu$/ Hz	T_c/K	$\Delta G^‡_{T_c}$/ kJ mol^{-1}	$\Delta H^‡_{298.2}$/ kJ mol^{-1}	$\Delta S^‡_{298.2}$/ J K^{-1} mol^{-1}
(5a)/(6a)	7	301	66.9	58.8 ± 0.6	-18.4 ± 2.1
(5b)	5	402	91.5		

A clue as to the structure of dissolved (5a) is given by its i.r. spectra in chloroform or acetonitrile. In both solvents a very strong and broad band centred at 2 070 cm^{-1} indicative of an isothiocyanate group is observed, and the absorptions at 1 530 and 1 600 cm^{-1} found in the i.r. spectrum of solid (5a) measured as KBr pellet are absent. However, after evaporation and resolidification the i.r. spectrum in KBr exhibits no absorption between 1 700 and 2 500 cm^{-1}, but again shows the bands of the original dipole (5a). From this i.r. spectroscopic evidence it appears that in solution no dipole (5a) is present, but that ring cleavage to give the valence tautomeric isothiocyanate (6a) has occurred. This transformation seems to take place immediately on dissolving (5a) and is fully reversible. According to the i.r. spectrum, the single crystal of (5a) used in the *X*-ray structural analysis was obtained from an acetonitrile solution containing only (6a).

In accordance with the i.r. spectroscopic evidence it seems probable that the $\Delta G^‡$ value determined for (5a) in solution (Table 4) is that for the topomerization around the C–N(Me$_2$) bond of the thioamide system in (6a). In fact, similar free-activation enthalpies were calculated for other compounds containing the structural unit $-C(Me_2)\cdot C(:S)\cdot NMe_2$.[3] However, considering the obviously low activation-energy for the equilibrium between (5a) and (6a) it is not possible to exclude the presence of small, spectroscopically insignificant amounts of the dipole (5a) and of the bicyclic compound (4a), where internal rotation around the C–NMe$_2$ bond should be essentially free. This would mean that the $\Delta G^‡$ value measured for dissolved (5a) characterizes the free activation enthalpy of the reaction of (5a) to give (4a) or of (6a) to give (5a) with the formation of (4a) being even faster.

Further insight into the nature of the dynamic process responsible for the measured $\Delta G^‡$ value should be provided by knowledge of the entropy of activation. For this reason a total lineshape analysis was carried out, the results of which are included in Table 4. The value of the entropy of activation falls within the range reported for hindered internal rotation around the partial CN double bond in amides and thioamides, where slightly negative $\Delta S^‡$ values are often found, though not well understood.[12] On the contrary, ring closure of (6a) to give (4a) *via* (5a) should be reflected by a significantly more negative $\Delta S^‡$ value and can be rejected.

Despite the close relations in the structure of crystalline (5a) and (5b) the behaviour of the two compounds in solution shows pronounced differences. While for (5b) the dipole is the thermodynamically stable species also in solution,[4] (5a) is transformed to (6a) on dissolving; (5a) or (4a) cannot be detected, (4a) also being kinetically insignificant. This valence tautomerism displayed by (5a) cannot be due to intramolecular effects, which should be operative both in the solid and in solution, but seems to stress the importance of intermolecular

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[10] E. Schaumann, A. Röhr, S. Sieveking, and W. Walter, *Angew. Chem. Internat. Edn.*, 1975, **14**, 493.

[11] W. Walter and J. Voß in J. Zabicky (ed.), 'The Chemistry of Amides,' Interscience, London, 1970, p. 383.

[12] W. Walter and E. Schaumann, *Chem. Ber.*, 1971, **104**, 3361, and references therein.

interactions for the stabilization of (5a) in the crystalline state (Figure 2). In contrast, the greater stability of (5b) in solution may be ascribed to some intramolecular charge compensation, which as in the crystal[4] is possible *via* the orientation of the negatively charged oxygen of the benzoyl residue towards the positively charged endocyclic sulphur atom. It may be noted that similar to (5a) intermolecular interactions strongly contribute to the stability of (7),[10] which, however, contrary to (5a) and (5b) predominates in polar solvents and gives increasing amounts of an uncharged species with decreasing solvent polarity.[13]

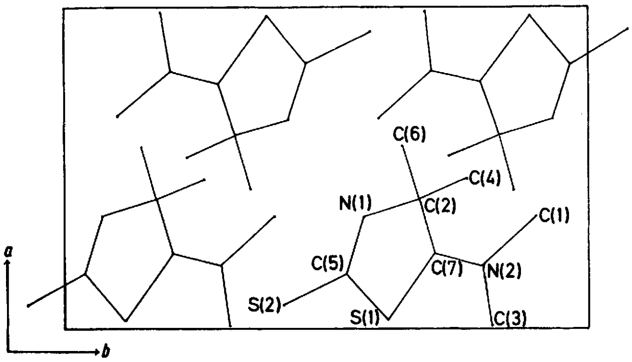

FIGURE 2 The contents of the unit cell as seen down the *c* axis

From the ease of reversion to the dipole (5a) on evaporation it may be concluded that the conformation of (6a) favours a nucleophilic attack of the thioamide sulphur atom at the carbon atom of the isothiocyanate moiety to give (5a). This reaction is without precedent between isolated isothiocyanates and thioamide molecules.

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[13] E. Schaumann, S. Sieveking, and W. Walter, *Tetrahedron*, 1974, **30**, 4147.