283. Crystal and Molecular Structure of *trans*-[(2-chlorophenyl)-1-benzocyclobutenyl]-1,4,5,6-tetrahydro-2-pyrimidyl-sulfide

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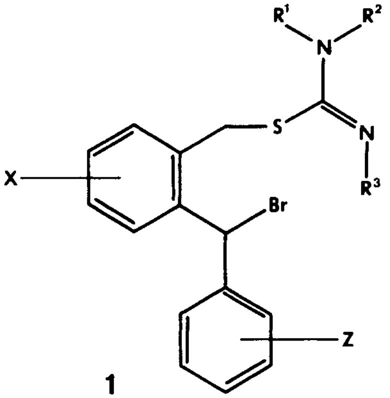
Kristalline und molekulare Struktur von *trans*-[(2-chlorphenyl)-1-benzocyclobutenyl]-(1,4,5,6-tetrahydropyrimidyl)-sulfid.

Zusammenfassung

Zur Abklärung von Konstitution und Konfiguration der Titelverbindung wurde eine Röntgenstrukturanalyse durchgeführt. Die Kristalle gehören zur monoklinen Raumgruppe *C2/c*, $a = 17.221(6)$, $b = 7.846(2)$, $c = 25.031(8)$ Å, $\beta = 104.55(2)°$, $Z = 8$. Die Struktur wurde mit 2188 signifikanten Daten bis $R = 0.055$ verfeinert. Die mittlere Standardabweichung der Lagekoordinaten der *C*- und *N*-Atome beträgt 0.003 Å.

In the study of the cyclisation reaction of thiouronium salts of the general type **1** to 5-aryl-2,4-benzothiazepines an unexpected product was obtained for X = H, Z = 2-Cl, $R^1 = H$, R^2, $R^3 = -(CH_2)_3-$ [1]. An X-ray analysis revealed this compound to be a *trans*-substituted benzo-cyclobutene, *i.e.* the title compound.



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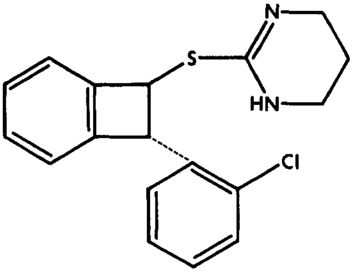

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Crystal Data. - $C_{18}H_{17}N_2SCl$, $M = 328$, colourless, prismatic crystals, grown from ether/petrolether solution, m.p. 102-105°, monoclinic, space group *C2/c*, $a = 17.221(6)$, $b = 7.846(2)$, $c = 25.031(8)$ Å, $\beta = 104.55\ (2)°$, $V = 3273.6$ Å^3, $d_{calc} = 1.33\ g \cdot cm^{-3}$, $Z = 8$, $\mu(CuK_\alpha) = 6.1\ cm^{-1}$.

Intensity Data. - Intensity profiles of reflexions were measured with a scintillation counter on a four-circle diffractometer (normal-beam equatorial method, crystal in bisecting position) with graphite monochromatized Cu*Ka* radiation ($\lambda = 1.542$ Å), ($\omega/2\theta$)-scan mode, variable scan width $\Delta\omega = 0.8° +$

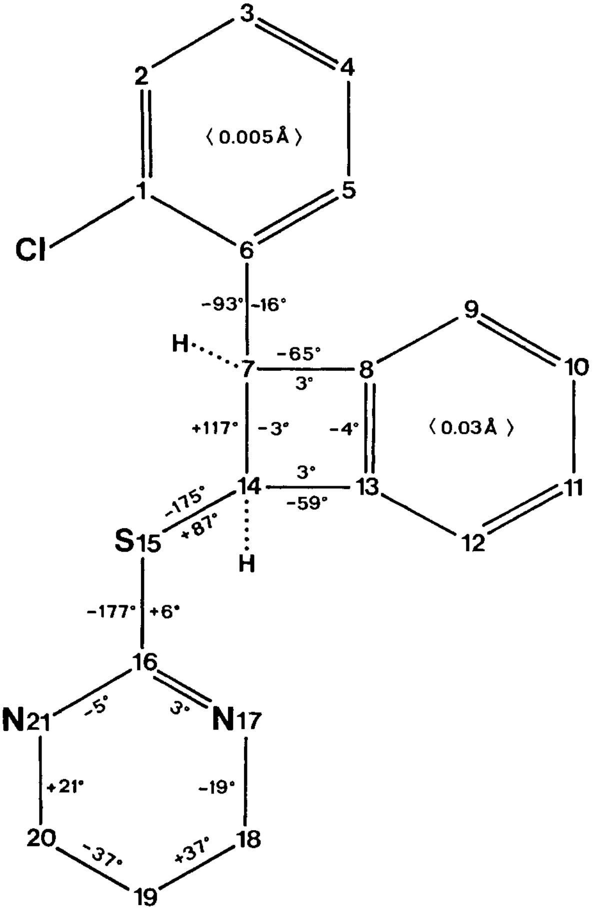

Fig. 1. *Numbering scheme of atoms and some torsion angles.* Mean e.s.d. of a torsion angle is 0.8°

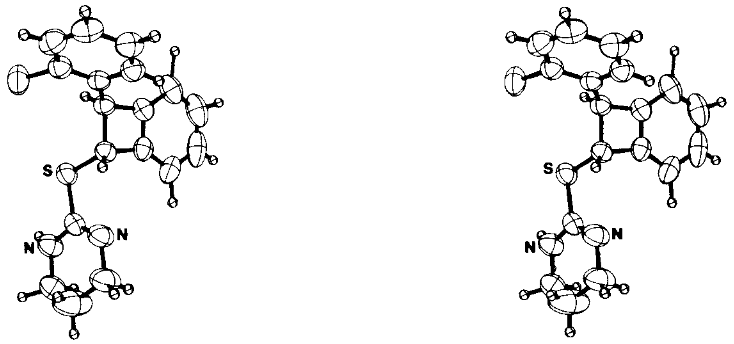

Fig. 2. *Stereoscopic projections of the molecule.* For the heavier atoms the 50%-probability thermal ellipsoids are drawn, the hydrogen atoms are uniformly drawn with a sphere corresponding to B = 1 Å^2

0.3 tan (θ), scan time adjusted so as to maintain a constant ratio of $\sigma(I)/I \approx 0.02$ (max. scan time 120 s). The profile counts were corrected for *Lorentz*-polarisation effects (but not for absorption, which was estimated to be less than 3%) and the net intensity evaluated by profile analysis [2]. The variance was calculated as $\sigma^2(I) = <I> + c^2I^2$, where $<I>$ is the variance based on a *Poisson* distribution of the measured counts, and c^2I^2 an intensity dependent term with an experimental $c = 0.02$.

The stability and orientation of the crystal during data collection was monitored by frequently remeasuring a number of check reflexions. 2439 unique reflexions within sin $(\theta)/\lambda < 0.56$ Å^{-1} were measured, and 2188 were judged to have significant intensity, *i.e.* $I \geqslant 2.5\ \sigma(I)$. Intensities were scaled to absolute structure amplitudes, $|F_o|$, by the *Wilson* method [3] and the variance of $|F_o|$ defined as $\sigma^2(F) = k\sigma^2(I)/4I$ (k = scale factor). The calculation of normalised $|E|$-values on the basis of an overall temperature factor $\bar{B} = 5.1$ Å^2 yielded the averages $<|E|> = 0.800$, $<|E^2 - 1|> = 0.968$, $<|E|^2> = 1.004$.

Structure Solution and Refinement. - An attempt to solve the structure by a symbolic addition procedure [4] failed. However, a detailed inspection of the *Patterson* function revealed the chlorine and sulfur positions, from which the positions of the remaining 20 atoms other than hydrogen were developed by successive calculation of structure factors and electron density maps.

The structure was refined by minimisation of $\sum w(|F_o| - kg'|F_c|)^2$ by the method of least-squares, using a block-diagonal approximation. The process was started with the refinement of a scale factor (k) and the coordinates of the non-hydrogen atoms, first with isotropic, then with anisotropic temperature factors. The positions of the hydrogen atoms were then calculated and included in the set of parameters, together with isotropic temperature factors. An isotropic extinction coefficient g' [5] was introduced in the final least-squares cycles. The weight function $w = 1/\sigma^2(F)$ was used for significant reflexions (w = O for significant reflexions). The refinement was terminated with an R = 0.055 for 2188 significant reflexions, with 260 structural parameters varied. The resulting atomic coordinates are given in *Table 1*, and the numbering of atoms is shown in *Fig. 1*. The average positional error is around 0.003 Å for *C*- and *N*-atoms, around 0.001 Å for Cl and S, and around 0.06 to 0.09 Å for H. The isotropic extinction coefficient g' reached a value of 8.6 (1.0) assuming a mean path length of 0.02 cm. Atomic scattering factors from "International Tables of Crystallography" (1962) were used in the structure-factor calculations. A list of the vibrational parameters and of the structure factors can be obtained from the authors.

Discussion. - The molecular conformation, with atoms represented by thermal vibration ellipsoids, is shown in stereoscopic projection in *Fig. 2*. Bond lengths and bond angles are given in *Tables 2* and *3*, and some torsion angles in *Fig. 1*. The benzocyclobutene moiety is approximately planar. The fourmembered ring shows a small but significant twist (see torsion angles, *Fig. 1*) and an appreciable lengthening of the C(7)–C(14) bond to 1.598 (4) Å (normal value for a $C(sp^3)-C(sp^3)$ is 1.542 Å).

The thiourea fragment is approximately planar (out of plane deformation of C(16) is 0.021 Å) and contains a double bond C(16)=N(17) of 1.275 (6) Å and a partial double bond C(16)$\stackrel{\cdot}{-}$N(21) of 1.337 (6) Å. The absence of any significant

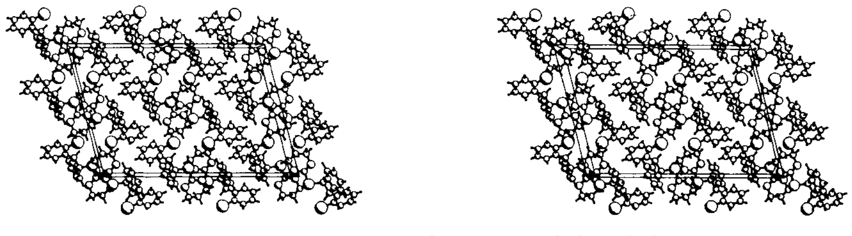

Fig. 3. *Stereoscopic packing diagram viewed along the* b-*axis*

residual density in the ΔF-map in the region of N(17), and the satisfactory refinement of the hydrogen on N(21) confirmed that in the crystal there is no tautomeric disorder of the proton between the two nitrogen atoms. The situation in solution is quite different, as evidenced by NMR. spectroscopy. In the ^{1}H-NMR. spectrum of the compound in $CDCl_3$ (see Exper. Part of [1]) the chemical shifts of the four protons on C(18) and C(20) coincide at 3,3 ppm, and the signals of the two protons on C(19) coincide at 1,8 ppm. These observations imply (i) fast exchange of the thiourea protons between the two nitrogen atoms, (ii) time-averaged C_{2v}-symmetry of the tetrahydropyrimidine ring, and (iii) rotation of the ring about the S(15)–C(16) bond. The first and third process may be coupled in a way to keep the double bond syn-periplanar to S(15)–C(14), as it is in the crystal. The tetrahydropyrimidine ring has an envelope conformation (see torsion angles in *Fig. 1*), but, as can be seen from *Fig. 2*, the thermal ellispoid of C(19) shows a strong

Table 1. *Fractional coordinates and e.s.d.'s.* The values for the heavier atoms are multiplied by 10^5, the ones for hydrogen atoms by 10^4

	x/a	*y/b*	*z/c*		*x/a*	*y/b*	*z/c*
Cl	75013(5)	15835(10)	41294(3)	C(20)	38605(23)	15687(44)	51777(13)
C(1)	70917(16)	19450(31)	34271(11)	N(21)	46147(16)	21350(33)	50712(9)
C(2)	73403(17)	8887(39)	30509(13)	H(2)	7651(17)	114(33)	3151(10)
C(3)	70322(17)	11273(44)	25037(12)	H(3)	7142(27)	345(56)	2207(17)
C(4)	64647(17)	23974(41)	23104(12)	H(4)	6258(17)	2518(35)	1925(11)
C(5)	62295(16)	34351(36)	26919(12)	H(5)	5848(18)	4440(44)	2616(12)
C(6)	65407(14)	32364(29)	32549(11)	H(7)	6736(15)	4655(32)	4017(10)
C(7)	62642(14)	43511(33)	36576(10)	H(9)	6541(27)	8288(47)	3073(18)
C(8)	58187(17)	59870(33)	34678(10)	H(10)	5194(21)	9876(43)	3060(15)
C(9)	59067(24)	75911(40)	32467(14)	H(11)	4232(18)	9026(40)	3388(11)
C(10)	52853(28)	86867(42)	32212(14)	H(12)	3923(19)	6267(43)	3724(14)
C(11)	46065(28)	82489(45)	34028(15)	H(14)	5159(15)	2677(32)	3660(10)
C(12)	45200(20)	66164(46)	36148(13)	H(181)	2925(33)	2791(38)	4162(31)
C(13)	51498(16)	55262(36)	36356(9)	H(182)	2974(20)	885(55)	3829(13)
C(14)	54657(15)	37749(34)	38217(10)	H(191)	2803(41)	567(60)	4774(40)
S(15)	56303(4)	32615(9)	45431(2)	H(192)	3560(52)	112(76)	4528(52)
C(16)	46570(16)	25236(31)	45585(10)	H(201)	4067(24)	725(56)	5559(17)
N(17)	41076(16)	23581(40)	41127(10)	H(202)	3634(59)	2978(74)	5271(39)
C(18)	33181(23)	17452(56)	41716(16)	H(21)	4954(21)	2388(41)	5313(13)
C(19)	33275(27)	9580(94)	46910(16)				

Table 2. *Bond lengths* (Å) *with e.s.d.'s*

Cl–C(1)	1.747(3)	C(7)–C(14)	1.598(4)	S(15)–C(16)	1.785(3)
C(1)–C(2)	1.401(4)	C(8)–C(9)	1.394(5)	C(16)–N(17)	1.275(4)
C(1)–C(6)	1.377(4)	C(8)–C(13)	1.367(4)	C(16)–N(21)	1.337(4)
C(2)–C(3)	1.347(5)	C(9)–C(10)	1.363(6)	N(17)–C(18)	1.485(5)
C(3)–C(4)	1.397(5)	C(10)–C(11)	1.404(6)	C(18)–C(19)	1.456(7)
C(4)–C(5)	1.393(4)	C(11)–C(12)	1.408(6)	C(19)–C(20)	1.420(7)
C(5)–C(6)	1.386(4)	C(12)–C(13)	1.380(5)	C(20)–N(28)	1.455(5)
C(6)–C(7)	1.504(4)	C(13)–C(14)	1.510(4)		
C(7)–C(8)	1.511(4)	C(14)–S(15)	1.801(3)		

Table 3. *Bond angles* (degrees) *with e.s.d.'s*

Cl–C(1)–C(2)	117.8(2)	C(9)–C(10)–C(11)	122.5(4)
Cl–C(1)–C(6)	120.3(2)	C(10)–C(11)–C(12)	121.7(4)
C(2)–C(1)–C(6)	121.9(3)	C(11)–C(12)–C(13)	114.7(4)
C(1)–C(2)–C(3)	119.4(3)	C(8)–C(13)–C(12)	122.8(3)
C(2)–C(3)–C(4)	120.9(3)	C(8)–C(13)–C(14)	94.3(2)
C(3)–C(4)–C(5)	118.7(3)	C(12)–C(13)–C(14)	142.8(3)
C(4)–C(5)–C(6)	121.5(3)	C(7)–C(14)–C(13)	85.7(2)
C(1)–C(6)–C(5)	117.6(3)	C(14)–S(15)–C(16)	100.5(2)
C(1)–C(6)–C(7)	121.9(3)	S(15)–C(16)–N(17)	120.4(2)
C(5)–C(6)–C(7)	120.5(3)	S(15)–C(16)–N(21)	111.9(2)
C(6)–C(7)–C(8)	120.3(3)	N(17)–C(16)–N(21)	127.7(3)
C(6)–C(7)–C(14)	116.3(2)	C(16)–N(17)–C(18)	116.2(3)
C(8)–C(7)–C(14)	85.5(2)	N(17)–C(18)–C(19)	115.1(4)
C(7)–C(8)–C(9)	142.3(3)	C(18)–C(19)–C(20)	118.0(5)
C(7)–C(8)–C(13)	94.4(2)	C(19)–C(20)–N(21)	111.3(4)
C(9)–C(8)–C(13)	123.1(3)	C(16)–N(21)–C(20)	120.8(3)
C(8)–C(9)–C(10)	115.2(4)		

anisotropy approximately perpendicular to the ring plane, suggesting that the atom has a large vibration amplitude in this direction even in the crystalline state.

The molecular packing in the crystal lattice is shown in *Fig. 3*. There are no unusually short intermolecular distances.

LITERATURE

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