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Abstract. The 5-nitro-2-tosylaminobenzaldehyde di(morpholin-4-yl)aminal forms a stable complex with carbon tetrachloride in the crystal phase. X-ray structural study of this complex indicates an essentially shortened intermolecular contact of 2.89 Å between the oxygen atom of the nitro group and one of the chlorine atom of the CCl_4 molecule. Quantum-chemical calculations by semiempirical AMI method showed that the formation of such complex did not cause considerable decrease of system energy or change of charge distribution in molecules. It was supposed that this associate has van der Waals character.

Introduction

Recently [1], it was found that 5-nitro-2-tosylaminobenzaldehyde di(morpholin-4-yl)aminal **1** forms the stable complex with carbon tetrachloride in the crystal phase.
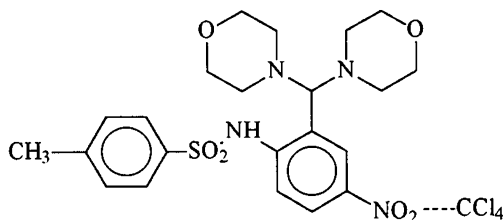
The aim of present work is the investigation of crystal and molecular structure of this compound.

Experimental part

The complex was synthesized according to our previous report [1].

Crystal data

$C_{22}H_{28}N_4O_6S$ CCl_4, $M_r = 630.35$, monoclinic, space group $P2_1/c$, $Z = 4$, $T = 293$ K, $a = 18.509(4)$ Å, $b = 8.465(2)$ Å, $c = 19.001(4)$ Å, $\beta = 110.56(2)°$, $V = 2787(1)$ Å^3, crystal size $0.4 \times 0.2 \times 0.1$ mm, $D_c = 1.502$ g/cm^3, $F(000) = 1304$, graphite-monochromated MoK_α radiation, $\lambda = 0.71073$ Å, $\mu = 0.55$ mm^{-1}. The intensities of 4863 reflections (4695 independent reflections, $R_{int} = 0.019$) were measured on a Siemens P3/PC diffractometer ($\theta - 2\theta$ scan, $2\theta_{max} = 50°$). The structure was solved by direct methods. The CCl_4 molecule is disordered over two positions with equal populations due to rotation around the C(1S)−Cl(1) bond. Calculated positions for the hydrogen atoms were refined with a riding model and fixed isotropic displacement parameters. Refinement against F^2 in anisotropic approximation by full-matrix least-squares method using 4635 reflections was performed to $wR2 = 0.100$ ($R1 = 0.043$, $wR2 = 0.090$ for 3579 reflections with $F > 4\sigma(F)$), $S = 1.086$. All calculations were carried out using SHELXTL PLUS 5.03 package [2]. Atomic coordinates, bond lengths and angles are listed in Tables 1–3, respectively.

Search for the crystal structures with NO ... Cl intermolecular contacts shorter than 3.2 Å was performed using Cambridge Crystal Structure Database [3]. Only structures with $R < 0.1$ were considered.

Quantum-chemical calculations were carried out by semi-empirical AM1 method [4] using MOPAC program.

Results and discussion

The *para*-nitroaniline fragment of complex is planar. The angle between planes of benzene ring and nitro group is 5.0(4)°. The morpholyl substituents have orthogonal and near to synclinal conformation with respect to the aromatic ring. The C(1)−C(2)−C(14)−N(4) and

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Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\mathring{A}^2 \times 10^3$) for complex. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U_{eq}
S(1)	1869(1)	2179(1)	3957(1)	21(1)
Cl(1)	5276(1)	11726(1)	3824(1)	37(1)
Cl(2)	5709(1)	14936(2)	3741(1)	58(1)
Cl(3)	5675(2)	12817(4)	2564(2)	86(1)
Cl(4)	6838(1)	12474(2)	4016(2)	68(1)
Cl(2′)	5417(3)	14831(5)	3288(3)	77(1)
Cl(3′)	5938(4)	12183(7)	2696(3)	60(1)
Cl(4′)	6771(3)	13187(8)	4194(3)	80(2)
O(1)	2353(1)	1287(2)	3656(1)	30(1)
O(2)	1065(1)	1800(2)	3739(1)	30(1)
O(3)	4269(1)	9548(2)	3209(1)	41(1)
O(4)	5069(1)	7589(2)	4486(1)	38(1)
O(5)	−338(1)	6807(2)	3922(1)	28(1)
O(6)	1473(1)	6941(2)	967(1)	32(1)
N(1)	1877(1)	4018(2)	3700(1)	20(1)
N(2)	4409(1)	8131(3)	4285(1)	26(1)
N(3)	960(1)	6658(2)	3426(1)	16(1)
N(4)	1408(1)	7328(3)	2425(1)	21(1)
C(1)	2519(1)	5011(3)	3828(1)	17(1)
C(2)	2386(1)	6630(3)	3670(1)	16(1)
C(3)	3018(1)	7629(3)	3838(1)	19(1)
C(4)	3760(1)	7028(3)	4127(1)	19(1)
C(5)	3898(1)	5440(3)	4247(1)	22(1)
C(6)	3278(1)	4421(3)	4105(1)	21(1)
C(7)	2286(1)	2126(3)	4946(1)	20(1)
C(8)	3040(1)	1615(3)	5295(1)	25(1)
C(9)	3355(2)	1628(3)	6073(2)	30(1)
C(10)	2929(2)	2130(3)	6506(2)	30(1)
C(11)	2172(2)	2600(3)	6140(2)	29(1)
C(12)	1845(1)	2608(3)	5365(1)	25(1)
C(13)	3287(2)	2165(5)	7355(2)	50(1)
C(14)	1598(1)	7377(3)	3234(1)	18(1)
C(15)	1053(1)	6999(3)	4217(1)	25(1)
C(16)	398(1)	6236(4)	4394(1)	29(1)
C(17)	−427(1)	6534(3)	3155(1)	25(1)
C(18)	204(1)	7302(3)	2949(1)	24(1)
C(19)	1899(2)	8332(3)	2156(1)	26(1)
C(20)	1548(2)	8457(3)	1310(2)	32(1)
C(21)	1007(2)	5952(3)	1230(1)	30(1)
C(22)	1345(2)	5780(3)	2084(1)	27(1)
C(1S)	5866(2)	12985(4)	3529(2)	35(1)

Table 2. Bond lengths ($\mathring{A}$) in structure of complex.

S(1)−O(2)	1.435(2)	N(4)−C(22)	1.448(3)
S(1)−O(1)	1.435(2)	N(4)−C(14)	1.452(3)
S(1)−N(1)	1.633(2)	N(4)−C(19)	1.460(3)
S(1)−C(7)	1.764(2)	C(1)−C(2)	1.406(3)
Cl(3)−C(1S)	1.753(3)	C(1)−C(6)	1.407(3)
Cl(2)−C(1S)	1.748(3)	C(2)−C(3)	1.386(3)
Cl(3)−C(1S)	1.747(4)	C(2)−C(14)	1.538(3)
Cl(4)−C(1S)	1.764(4)	C(3)−C(4)	1.385(3)
Cl(2′)−C(1S)	1.754(5)	C(4)−C(5)	1.373(4)
Cl(3′)−C(1S)	1.769(7)	C(5)−C(6)	1.383(4)
Cl(4′)−C(1S)	1.716(6)	C(7)−C(8)	1.387(3)
O(3)−N(2)	1.225(3)	C(7)−C(12)	1.387(4)
O(4)−N(2)	1.233(4)	C(8)−C(9)	1.387(4)
O(5)−C(17)	1.426(3)	C(9)−C(10)	1.390(4)
O(5)−C(16)	1.427(3)	C(10)−C(11)	1.387(4)
O(6)−C(21)	1.413(3)	C(10)−C(13)	1.514(4)
O(6)−C(20)	1.424(3)	C(11)−C(12)	1.381(4)
N(1)−C(1)	1.405(3)	C(15)−C(16)	1.513(4)
N(2)−C(4)	1.467(3)	C(17)−C(18)	1.504(3)
N(3)−C(18)	1.479(3)	C(19)−C(20)	1.512(4)
N(3)−C(15)	1.480(3)	C(21)−C(22)	1.527(3)
N(3)−C(14)	1.482(3)		

Table 3. Bond angles (deg.) in structure of complex.

O(2)−S(1)−O(1)	119.8(1)	C(12)−C(7)−S(1)	118.6(2)
O(2)−S(1)−N(1)	104.2(1)	C(7)−C(8)−C(9)	118.9(2)
O(1)−S(1)−N(1)	108.1(1)	C(8)−C(9)−C(10)	121.3(2)
O(2)−S(1)−C(7)	108.9(1)	C(11)−C(10)−C(9)	118.4(2)
O(1)−S(1)−C(7)	108.0(1)	C(11)−C(10)−C(13)	121.0(3)
N(1)−S(1)−C(7)	107.2(1)	C(9)−C(10)−C(13)	120.7(3)
C(17)−O(5)−C(16)	109.3(2)	C(12)−C(11)−C(10)	121.5(2)
C(21)−O(6)−C(20)	110.3(2)	C(11)−C(12)−C(7)	119.1(2)
C(1)−N(1)−S(1)	127.9(2)	N(4)−C(14)−N(3)	109.4(2)
O(3)−N(2)−O(4)	123.2(2)	N(4)−C(14)−C(2)	112.9(2)
O(3)−N(2)−C(4)	118.3(2)	N(3)−C(14)−C(2)	112.7(2)
O(4)−N(2)−C(4)	118.5(2)	N(3)−C(15)−C(16)	109.0(2)
C(18)−N(3)−C(15)	107.4(2)	O(5)−C(16)−C(15)	112.2(2)
C(18)−N(3)−C(14)	111.2(2)	O(5)−C(17)−C(18)	111.9(2)
C(15)−N(3)−C(14)	110.6(2)	N(3)−C(18)−C(17)	109.7(2)
C(22)−N(4)−C(14)	116.8(2)	N(4)−C(19)−C(20)	109.0(2)
C(22)−N(4)−C(19)	109.4(2)	O(6)−C(20)−C(19)	111.1(2)
C(14)−N(4)−C(19)	113.9(2)	O(6)−C(21)−C(22)	111.0(2)
N(1)−C(1)−C(2)	118.2(2)	N(4)−C(22)−C(21)	109.1(2)
N(1)−C(1)−C(6)	121.7(2)	Cl(3)−C(1S)−Cl(2)	109.2(2)
C(2)−C(1)−C(6)	120.1(2)	Cl(4′)−C(1S)−Cl(1)	112.5(3)
C(3)−C(2)−C(1)	118.4(2)	Cl(3)−C(1S)−Cl(1)	111.5(2)
C(3)−C(2)−C(14)	115.9(2)	Cl(2)−C(1S)−Cl(1)	109.1(2)
C(1)−C(2)−C(14)	125.3(2)	Cl(4′)−C(1S)−Cl(2′)	110.8(3)
C(4)−C(3)−C(2)	120.4(2)	Cl(1)−C(1S)−Cl(2′)	109.5(2)
C(5)−C(4)−C(3)	121.7(2)	Cl(3)−C(1S)−Cl(4)	109.0(2)
c(5)−C(4)−N(2)	119.2(2)	Cl(2)−C(1S)−Cl(4)	109.4(2)
C(3)−C(4)−N(2)	118.3(2)	Cl(1)−C(1S)−Cl(4)	108.6(2)
C(4)−C(5)−C(6)	119.0(2)	Cl(4′)−C(1S)−Cl(3′)	109.6(3)
C(5)−C(6)−C(1)	120.1(2)	Cl(1)−C(1S)−Cl(3′)	107.7(3)
C(8)−C(7)−C(12)	120.9(2)	Cl(2′)−C(1S)−Cl(3′)	106.6(3)
C(8)−C(7)−S(1)	120.5(2)		

C(1)−C(2)−C(14)−N(3) torsion angles are −84.9(4)° and 39.5(4)°, respectively. Such orientation of the dimorpholylmethyl group is determined by the intramolecular hydrogen bond N(3)...H(1)−N(1) (N...H 2.06(4) Å, N...H−N 156(2)°). Saturated heterocycles have an almost ideal chair conformation. The range of the absolute values of endocyclic torsion angle is 57.7°−60.0°. The sulphur atom is almost coplanar with the benzene ring, the C(6)−C(1)−N(1)−S(1) torsion angle being 10.5(4)°. The tolyl group has synclinal conformation with respect to the C(1)−N(1) bond (the C(1)−N(1)−S(1)−C(7) torsion angle is 60.0(4)°) and near to an orthogonal orientation relatively to the S(1)−N(1) bond (the N(1)−S(1)−C(7)−C(8) torsion angle is −102.4(4)°).

The N(1) atom has trigonal-pyramidal configuration and the sum of the bond angles is 355.3°. Such configuration is not usual and it is caused, probably, by the formation of the intramolecular hydrogen bond mentioned above and the shortened contact S(1)...H(6) 2.83(3) Å (van der Waals radii sum is 3.00 Å [5]).

Table 4. Geometrical characteristics of the C−Cl...O−N short intermolecular contacts

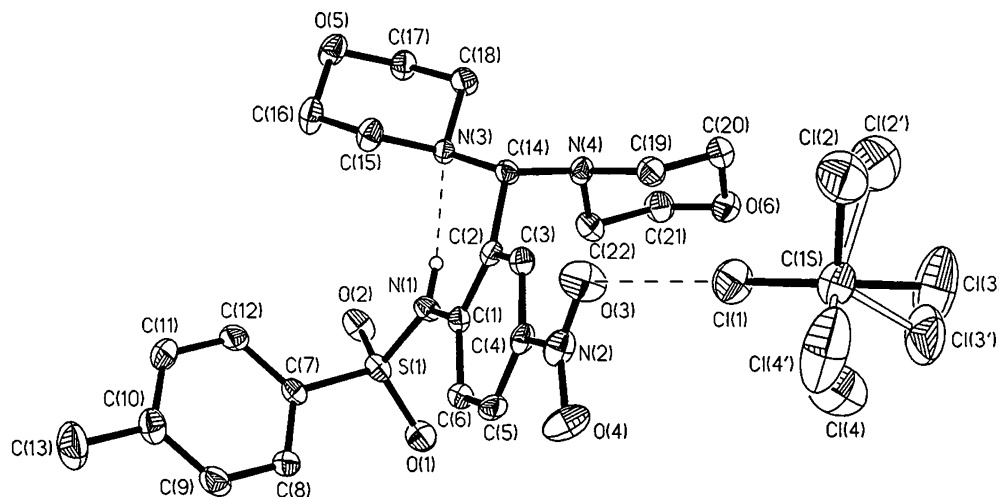| Cl...O, Å	C−Cl...O, deg	Cl...O−N, deg	C−Cl...O−N, deg	References
2.89	176.1	121.7	69.0	present work
3.18	152.0	115.9	30.4	[6]
2.97	171.3	116.5	−151.4	[7]
2.98	164.8	160.9	43.1	[8]

Fig. 1. General view of complex with atomic numbering. Thermal ellipsoids are presented as 50% probability surfaces. Hydrogen atoms are omitted for clarity excepts for NH group.

The main feature of the considered crystal structure is an extra short intermolecular contact O(3)...Cl(1) of 2.89(1) Å (van der Waals radii sum is 3.19 Å). The presence of such contact and the fixed position of this chlorine atom as compared with the other disordered atoms allow to suppose the possibility of some attractive interactions between nitro group and CCl₄ molecule.

A search in Cambridge Crystal Structure Database revealed three crystal structures with the N−O ... Cl intermolecular contact shorter than 3.2 Å. Geometrical characteristics of these contacts are listed in Table 4. Proceeding from these data we can only say that a shorter Cl ... O distance causes an increase of the C−Cl ... O angle.

In order to understand the nature of the considered interaction we performed quantum-chemical calculations for molecule 1 and some other aliphatic and aromatic nitro compounds and their associates with CCl₄. Obtained data indicate that the complex formation does not entail considerable decrease of the system energy. Differences between the heats of formation for isolated and associated molecules are smaller than 0.2 kcal/mol. Moreover, we did not find any significant change of the atomic charges distribution. Computed bond order and orbital overlap populations between the oxygen and chlorine atoms are zero. Thus, the results of quantum-chemical calculations do not permit to make a definite conclusion about the presence of strong attractive interaction between nitro group and carbon tetrachloride molecule.

Nevertheless, this shortened contact can be explained on the basis of the high polarizability ($116.83 \cdot 10^{-41}$ C^2m^2/J [9, 10]) of the CCl_4 molecule under action of a large negative charge of the oxygen atom. For comparison this value for ethylene and carbon dioxide is much smaller ($47.4 \cdot 10^{-41}$ and $24.49 \cdot 10^{-41}$ C^2m^2/J [9, 10]). Therefore

we can suppose the presence of charge-induced charge interaction between these atoms. Similar interactions are usual for van der Waals complexes [9].

Thus, associate of molecule 1 and carbon tetrachloride observed in the crystal phase, probably, has van der Waals character.

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