Structure and spectroscopic properties of 2,4-dichloro-1-diethylamino-3,5-diphenyl-1,3-pentadien-5-one, the product of the unusual reaction of triethylamine with (dibenzoylmethanato)antimony tetrachloride

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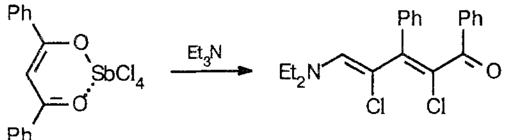
The crystal and molecular structures of the title compound have been established by the X-ray diffraction method. The molecule has a bent configuration with a dihedral angle between the double bond planes of 43.2°. The double bonds are localized and have lengths of 1.351(6) and 1.355(6) Å. However vibrational and electronic spectroscopy indicate that the conjugation in the butadiene fragment is retained; this fragment is a conductor of the direct polar conjugation effect between the donor diethylamino group and the acceptor carbonyl group.

Key words: 2,4-dichloro-1-diethylamino-3,5-diphenyl-1,3-ppentadien-5-one, crystal and molecular structure, electronic and vibrational spectra, mass spectra, π-conjugation.

Previously we described[1] the reaction of excess triethylamine with (dibenzoylmethanato)antimony tetrachloride resulting in the substituted butadiene **1** in a low yield:



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The reaction is unusual in that a new C—C bond is formed between the β-carbon atom of one of the ethyl groups of triethylamine and the carbonyl carbon atom under mild conditions (suspension of **1** in a mixture of ether and triethylamine). The mechanism of this reaction is still unknown.

In this work we present the results of physicochemical investigations of butadiene **1** by the X-ray diffraction method, mass spectrometry, and vibrational and electronic spectroscopy.

The general view of molecule **1** is shown in Fig. 2, and its bond lengths and bond angles are given in Tables 1 and 2, respectively. According to the X-ray structural data, molecule **1** has *E*- and *Z*-configurations of the C(2)=C(3) and C(4)=C(5) bonds, respectively. The structures of polyene derivatives with electron-donor and electron-acceptor groups at the opposite termini of the polyene chain, such as ω-dimethylaminocarbonyl polyenes (merocyanines) $Me_2N(CH{=}CH)_{n-1}{-}CH{=}CHXY$ (X, Y = COOMe, COMe, CN, *n* = 2, 3, 4) (**2**) and bis-ω,ω'-diamino ketones, the simplest representative of which is $Me_2N(CH{=}CH)_2{-}CO{-}(CH{=}CH)_2NMe_2$ (**3**),[2–4] have been described in the literature. Considerable delocalization over the bonds in the planar polyene chain is typical of these compounds. Thus, in molecule **2** with X = Y = COMe and *n* = 2,

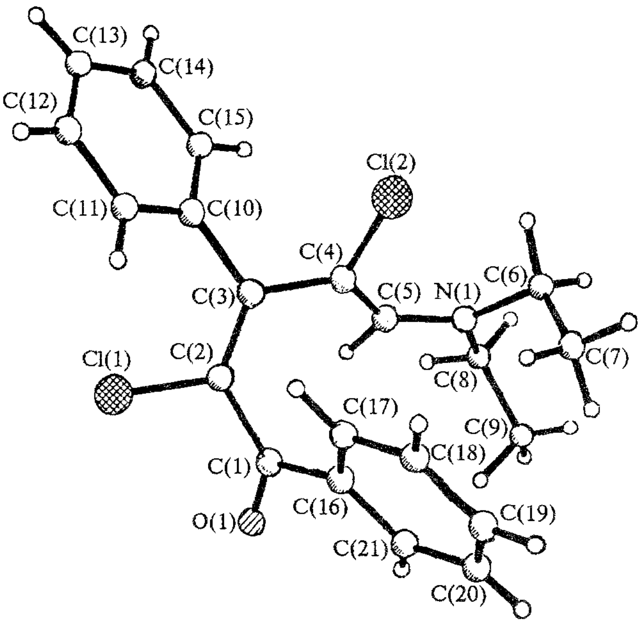

Fig. 1. Molecular structure of 2,4-dichloro-1-diethylamino-3,5-diphenyl-1,3-pentadien-5-one (**1**).

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Table 1. Bond lengths (*d*) in molecule **1**

Bond	*d*/Å	Bond	*d*/Å
Cl(1)—C(2)	1.756(4)	C(8)—C(9)	1.471(9)
Cl(2)—C(4)	1.750(4)	C(10)—C(11)	1.387(7)
O(1)—C(1)	1.221(5)	C(10)—C(15)	1.386(6)
N(1)—C(5)	1.343(6)	C(11)—C(12)	1.382(7)
N(1)—C(6)	1.482(6)	C(12)—C(13)	1.368(8)
N(1)—C(8)	1.465(6)	C(13)—C(14)	1.368(9)
C(1)—C(2)	1.490(6)	C(14)—C(15)	1.388(6)
C(1)—C(16)	1.499(5)	C(16)—C(17)	1.385(5)
C(2)—C(3)	1.351(6)	C(16)—C(21)	1.389(6)
C(3)—C(4)	1.454(6)	C(17)—C(18)	1.389(6)
C(3)—C(10)	1.503(5)	C(18)—C(19)	1.376(8)
C(4)—C(5)	1.355(6)	C(19)—C(20)	1.376(7)
C(6)—C(7)	1.494(8)	C(20)—C(21)	1.385(7)

Table 2. Bond angles (ω) in molecule **1**

Angle	ω/deg	Angle	ω/deg
C(5)—N(1)—C(6)	125.5(4)	N(1)—C(8)—C(9)	114.7(5)
C(5)—N(1)—C(8)	118.3(4)	C(3)—C(10)—C(11)	120.5(4)
C(6)—N(1)—C(8)	116.2(4)	C(3)—C(10)—C(15)	120.1(4)
O(1)—C(1)—C(2)	120.5(3)	C(11)—C(10)—C(15)	119.4(4)
O(1)—C(1)—C(16)	119.3(4)	C(10)—C(11)—C(12)	120.0(5)
C(2)—C(1)—C(16)	119.9(3)	C(11)—C(12)—C(13)	120.5(5)
Cl(1)—C(2)—C(1)	112.3(3)	C(12)—C(13)—C(14)	120.0(5)
Cl(1)—C(2)—C(3)	120.5(3)	C(13)—C(14)—C(15)	120.5(5)
C(1)—C(2)—C(3)	127.1(4)	C(10)—C(15)—C(14)	119.7(5)
C(2)—C(3)—C(4)	119.0(4)	C(1)—C(16)—C(17)	123.1(4)
C(2)—C(3)—C(10)	122.4(4)	C(1)—C(16)—C(21)	117.5(3)
C(4)—C(3)—C(10)	118.4(3)	C(17)—C(16)—C(21)	119.3(4)
Cl(2)—C(4)—C(3)	115.2(3)	C(16)—C(17)—C(18)	120.5(4)
Cl(2)—C(4)—C(5)	124.6(3)	C(17)—C(18)—C(19)	119.4(4)

the C—C bond lengths in the butadiene fragment are nearly the same: 1.395, 1.405, and 1.378 Å; the C—N bond length (1.322 Å, see Ref. 2) is significantly smaller than the normal value (1.43 Å). Unlike these compounds, molecule **1**, also bearing substituents of different nature at the opposite termini of the butadiene system, is essentially nonplanar, and the double bonds in **1** are localized. Obviously, the main reason for the distortion of the butadiene chain from planarity is the steric overcrowding of the molecule. However, despite the nonplanar conformation of the molecule, the shortened intramolecular contacts between the substituents are retained, *e.g.*, Cl(1)···C(11) 3.271(5), Cl(2)···C(10) 3.134(5), Cl(2)···C(6) 3.192(5), C(1)···C(5) 3.025(6), C(4)···C(6) 3.133(6) Å. The mutual repulsion of the substituents is so strong, that it causes significant twisting of the molecule not only about the ordinary bonds, but also about the C(2)=C(3) double bond (the C(1)—C(2)—C(3)—C(4) torsion angle is 18.2°, see Table 3) in addition to an increase in the bond angles at the C(2), C(4), and C(5) atoms. The C—Cl and C=C bonds are slightly longer than the normal bonds (1.734 and 1.330 Å, respectively, see Ref. 5), while the C(5)—N(1) and C(3)—C(4) bonds are slightly shorter. The other geometrical parameters of molecule **1** have normal values. There are no short intermolecular contacts in the structure of **1**.

Based on the structural data, a significant decrease in conjugation between the double bonds of the butadiene fragment, as compared with the molecules with the planar butadiene fragment, can be suggested. It is assumed that the energy of conjugation is proportional to $\cos^2\varphi$ (φ is the dihedral angle formed by the double-bond planes). Then the conjugation energy in the butadiene fragment of molecule **1** amounts to ~50% of the conjugation energy in molecules **2** and **3**, in which the double bonds are coplanar.

The sensitivity of spectroscopic characteristics to conjugation effects is well known.[6] The electronic and Raman spectra of solid **1** were recorded and compared with those of **2** and **3** published in Refs. 7—9. The Raman spectra of solid samples of **1** and **3** (Fig. 2) are very similar, despite the difference in the structures of these compounds. Both spectra are characterized by an intense ν(C=C) band in the region of 1520—1530 cm^{-1} and a weak ν(C=O) band in the region of 1630—1640 cm^{-1}. The Raman spectra of compounds **1** and **3** are distinctly different from those of compounds with nonconjugated double bonds; in the spectra of the latter, the bands in the 1680—1640 cm^{-1} region correspond to the ν(C=C) stretching vibrations (see Ref. 10). Simple nonpolar conjugation between the double bonds results in the lowering of the ν(C=C) frequencies to

Table 3. Selected torsion angles (φ) in molecule **1**

Angle	φ/deg	Angle	φ/deg	Angle	φ/deg
O(1)—C(1)—C(2)—Cl(1)	31.8	C(6)—N(1)—C(8)—C(9)	69.7	Cl(2)—C(4)—C(3)—C(10)	45.8
O(1)—C(1)—C(2)—C(3)	−144.1	C(2)—C(3)—C(10)—C(11)	54.6	C(5)—C(4)—C(3)—C(2)	43.2
C(16)—C(1)—C(2)—Cl(1)	−143.1	C(4)—C(3)—C(10)—C(11)	−130.9	C(5)—C(4)—C(3)—C(10)	−131.5
C(16)—C(1)—C(2)—C(3)	41.0	C(2)—C(3)—C(10)—C(15)	−124.0	C(6)—N(1)—C(5)—C(4)	12.3
C(4)—C(3)—C(2)—Cl(1)	−157.3	C(4)—C(3)—C(10)—C(15)	50.5	C(8)—N(1)—C(5)—C(4)	−169.7
C(4)—C(3)—C(2)—C(1)	18.2	C(17)—C(16)—C(1)—O(1)	−149.7	N(1)—C(5)—C(4)—Cl(2)	5.1
C(10)—C(3)—C(2)—Cl(1)	17.1	C(17)—C(16)—C(1)—C(2)	25.3	N(1)—C(5)—C(4)—C(3)	−177.8
C(10)—C(3)—C(2)—C(1)	−167.3	C(21)—C(16)—C(1)—O(1)	26.2	C(7)—C(6)—N(1)—C(5)	72.4
Cl(2)—C(4)—C(3)—C(2)	−139.5	C(21)—C(16)—C(1)—C(2)	−158.8	C(7)—C(6)—N(1)—C(8)	−105.7
C(5)—N(1)—C(8)—C(9)	−108.5				

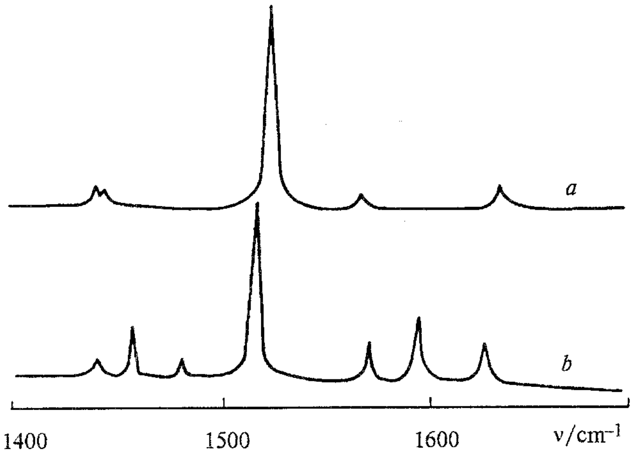
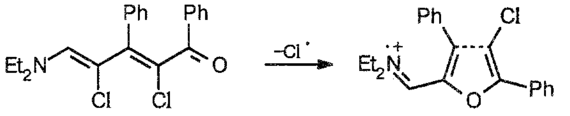


Fig. 2. The Raman spectra of dienic bis-ω,ω'-diamino ketone **3**, laser excitation wavelength 647.1 nm (see Ref. 7) (*a*), and 1,4-dichloro-1-diethylamino-3,5-diphenyl-1,3-pentadien-5-one (**1**), laser excitation wavelength 647.1 nm (*b*).

1650—1590 cm^{-1}. In the spectrum of *trans*-butadiene, the frequencies of the symmetric and asymmetric ν(C=C) stretching vibrations are 1643 and 1597 cm^{-1}, respectively.[11] Attachment of the Cl atom to the double bond slightly affects the ν(C=C) frequencies. In the Raman spectrum of chloroprene, the bands at 1629 and 1590 cm^{-1} correspond to these stretching vibrations (see Ref. 11). Increasing the length of the chain of conjugation results in further lowering of the ν(C=C) stretching frequencies. In the Raman spectra of compounds with a large number of conjugated double bonds, such as β-carotene, and in the spectra of ω-dimethylaminocarbonyl polyenes **2** and **3**, in which the effect of conjugation is enhanced by the electron interactions of the donor and acceptor groups at the opposite termini of the polyene chain (direct polar conjugation), the intense band of symmetric ν(C=C) stretching vibration was observed in the abnormally low region of 1520—1550 cm^{-1} (see Ref. 7). The appearance of the intense ν(C=C) band at 1520 cm^{-1} in the Raman spectrum of **1** indicates the retention of conjugation in the butadiene fragment. This conclusion was confirmed by the analysis of the electronic spectrum of **1**. In the visible region of the spectrum, a broad band was observed with a maximum at 470 nm and a shoulder at ~420 nm, which is typical of the spectra of highly conjugated systems, such as **2** with $n \geq 3$ and **3** (see Ref. 7).

From the data discussed above, it follows that compound **1** is an interesting example of a molecule with a nonplanar butadiene fragment and weakly delocalized C—C bonds, which, however, exhibits spectroscopic characteristics typical of butadienes with donor and acceptor groups at the opposite termini of the butadiene chain and with the π-electron density delocalized along the whole chain of conjugation. In the mass spectrum of **1** the molecular ion peak was absent. The heaviest and the most abundant peak was that of the $[M—Cl]^+$ ion (*m/z* 338/340), which essentially did not undergo further fragmentation, indicating its high stability.

It is believed that this is due to the formation of a stable furan system:



Another pathway of fragmentation of **1** under electron impact resulted in the $PhCO^+$ (*m/z* 105, 13 %) and Ph^+ (*m/z* 77, 16 %) ions.

Experimental

Crystals of **1** ($C_{21}H_{21}Cl_2NO$) are monoclinic, with the following unit-cell parameters at 20 °C: a = 9.568(2), b = 23.146(5), c = 9.154(2) Å, β = 106.14(2), Z = 4, the space group $P2_1/c$. The unit-cell parameters and intensities of 2406 independent reflections, 1792 of which with $I \geq 4\sigma'$ were used for solving and refining the structure, were measured on a Siemens P3/PC diffractometer (λ(Mo-Kα), graphite monochromator, θ/2θ-scan technique, θ ≤ 30). The structure was solved by direct methods and refined by the full-matrix least-squares method with anisotropic temperature factors for all nonhydrogen atoms. The H atoms were located from the difference electron density map, refined isotropically with the constant value of U = 0.05 $Å^2$. The final values of the R factors were R = 0.042, R_w = 0.042; all calculations were carried out on a IBM PC/AT computer with the SHELX PLUS program package.

The Raman spectrum of the solid-state samples of **1** was recorded on a Ramanor-HG-2S spectrometer with a Kr^+ laser (6471 Å, laser power 50 mW). The IR spectrum of solid **1** in KBr was recorded on a Bruker IFS-25 Fourier-transform infrared spectrometer with 2-cm^{-1} resolution. The IR spectrum in the region of 1400—1700 cm^{-1} showed bands at 1633 s (ν(C=C)), 1601 s, 1594 s (ν Ph), 1574 m (ν(C=C)), 1518 m (ν(C=C)), 1487 w (ν Ph), 1455 s (δ Et), and 1422 w (δ Et) cm^{-1}. The electronic spectrum was obtained on a Specord M-40 spectrometer using solid samples in vaseline oil placed between KBr plates. The mass spectrum was recorded on a VG Analytical 7070E instrument with ionizing electron beam energy 70 eV, the ion source temperature was 150 °C.

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