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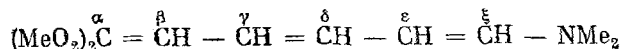
CRYSTALLINE AND ELECTRONIC STRUCTURES OF THE METHYL ESTER OF TRANS-7-DIMETHYLAMINO-2-CARBOMETHOXYHEPTATRIENECARBOXYLIC ACID

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UDC 541.6:547.316.6

The present work is a continuation of our earlier studies on conjugation effects and atomic interactions in $(\text{MeO}_2\text{C})_2\text{C}=\text{CH}-(\text{HC}=\text{CH})_n-\text{NMe}_2$ conjugated systems.

The crystalline and electronic structures of the methyl ester of trans-5-dimethylamino-2-carbomethoxypentadienecarboxylic acid ($n = 1$) (I) have been described in [1]. In the present work, x-ray studies and quantum-chemical calculations have been carried out on the methyl ester of trans-7-dimethylamino-2-carbomethoxyheptatrienecarboxylic acid ($n = 2$) (II) [2].



EXPERIMENTAL

Ester (II) was crystallized from a mixed hexane-acetone solution, appearing in the form of reddish violet sheets. The compound is known to belong to the monoclinic crystal system, the space group and unit cell parameters having been determined in previous studies of rotation and Weissenberg x-ray diagrams. The cell parameters were refined by a least-squares treatment of the results of 40 diffraction measurements on the Hilger-Watts diffractometer: $a = 7.78_6$; $b = 15.59_7$; $c = 10.88_1$ Å; $\beta = 102.27_2^\circ$; $M = 239$; $V = 1292$ Å³; $d_{\text{calc}} = 1.24$; space group $P2_1/n$, $N = 4$.^{*} This same diffractometer was used to measure reflection intensities through the Hilger program $\theta \leq 57^\circ$ (Cu K_α radiation, graphite monochromator, $\theta/2\theta$ scanning). Elimination of the reflections with $J(hk\ell) \leq 3\sigma$, left 1175 F (hk ℓ) reflections. Absorption was not considered in the calculations.

^{*}N was determined from the equation $N = V/18$ [3].

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 8, pp. 1742-1747, August, 1979. Original article submitted April 10, 1978.

TABLE 1. Coordinates and Anisotropic Parameters for the Various Atoms $T = \exp[-b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl]$

Atom	X	Y	Z	$\times 10^4$					
				b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
O ¹	0.9073(4)	0.3123(2)	0.3155(3)	289	44	190	26	2	-38
O ²	0.4520(3)	0.5005(2)	0.1518(3)	230	59	223	14	23	3
N ³	1.4296(4)	0.6954(2)	0.4945(3)	191	51	172	-16	37	-4
C ⁴	0.6910(4)	0.4103(2)	0.2245(3)	207	43	124	-24	85	-7
O ⁵	0.6992(5)	0.2646(2)	0.1659(4)	398	58	281	23	-155	-72
C ⁶	1.0340(4)	0.5731(2)	0.3558(4)	238	47	136	-13	82	7
C ⁷	0.7872(4)	0.4820(2)	0.2670(3)	217	42	104	4	97	3
C ⁸	0.9664(5)	0.4934(2)	0.3205(4)	217	41	153	-12	61	4
C ⁹	1.2107(4)	0.5904(2)	0.4064(4)	207	42	124	-11	41	10
O ¹⁰	0.4025(4)	0.3630(2)	0.1365(4)	252	67	372	-28	-105	-31
C ¹¹	0.5054(5)	0.4195(2)	0.1654(4)	233	46	128	-29	59	-27
C ¹²	1.2668(4)	0.6719(2)	0.4411(4)	210	48	161	-7	81	-3
C ¹³	0.7596(5)	0.3237(2)	0.2292(4)	200	43	138	-23	1	-20
C ¹⁴	1.4695(6)	0.7831(3)	0.5364(5)	307	64	249	-35	9	-37
C ¹⁵	1.5719(5)	0.6338(3)	0.5210(5)	222	72	233	17	32	51
C ¹⁶	0.2708(5)	0.5151(3)	0.0946(5)	275	93	236	52	38	6
C ¹⁷	0.9850(6)	0.2282(3)	0.3305(5)	353	63	235	59	8	-2
H ¹⁸	1.1790	0.722	0.443						
H ¹⁹	0.717	0.542	0.266						
H ²⁰	1.040	0.442	0.327						
H ²¹	0.942	0.628	0.348						
H ²²	1.305	0.537	0.410						
H ²³	1.553	0.562	0.517						
H ²⁴	1.358	0.823	0.521						
H ²⁵	0.257	0.580	0.053						
H ²⁶	1.076	0.227	0.424						
H ^{27*}	1.526	0.784	0.636						
H ^{28*}	1.563	0.810	0.486						
H ^{29*}	1.649	0.647	0.613						
H ^{30*}	1.654	0.647	0.452						
H ^{31*}	0.227	0.467	0.020						
H ^{32*}	0.188	0.508	0.163						
H ^{33*}	0.884	0.179	0.323						
H ^{34*}	1.057	0.216	0.255						

*H atoms located theoretically (see also Tables 2 and 3).

The structure was deduced by the so-called direct method, using the algorithm of [4, 5]. An E synthesis localized all of the nonhydrogen atoms ($R = 0.25$), and the coordinates of these atoms were then refined by two successive ρ syntheses. Further refinement to $R = 0.102$ was obtained through a least-squares treatment, first in the isotropic, and then in the anisotropic approximation; further refinement through a difference synthesis fixed the coordinates of all of the H atoms with exception of the eight involved in the CH_3 groups. The coordinates of the H atoms which had been located at this stage were refined by two successive ρ syntheses. The final value of R was 0.079. Table 1 gives coordinates and thermal parameters for the C, O, and N atoms. The coordinates of the H atoms represent values obtained from the ρ synthesis of the last difference series.

DISCUSSION OF RESULTS

The molecular geometry of compound (II) is shown in Fig. 1. Bond lengths and values of the valence angles are given in Tables 2 and 3. With exception of the carbomethoxy groups which make angles of 10° (plane II) and 24° (plane III) with the basic plane of the molecule (plane I), the molecule of (II) is planar. Values of the dihedral angles are shown in Table 4. The triene system of the molecule has the α - β , γ - δ , and ϵ - ζ double bonds in s-trans configuration, and the H atoms at the β - γ , and δ - ϵ bonds in trans configuration. The two CO groups and the α - β bond are in s-trans conformation. It is interesting to note that although the diene system of (I), which we studied earlier, showed this same s-trans arrangement of double bonds, and trans arrangement of the H atoms at the double bonds, the CO groups and the α - β double bond were there in s-cis conformation.

The N atom is in sp^2 hybridization; the length of the $\text{N}^3\text{-C}^{12}$ single bond (1.329 Å) is close to the length of the C-N bond in (I) (1.338 Å). The triene C-C bonds alternate in length ($\text{C}^4\text{-C}^7$ 1.371; $\text{C}^7\text{-C}^8$ 1.405; $\text{C}^8\text{-C}^6$ 1.372; $\text{C}^6\text{-C}^9$ 1.395, and $\text{C}^9\text{-C}^{12}$ 1.372 Å), just as in

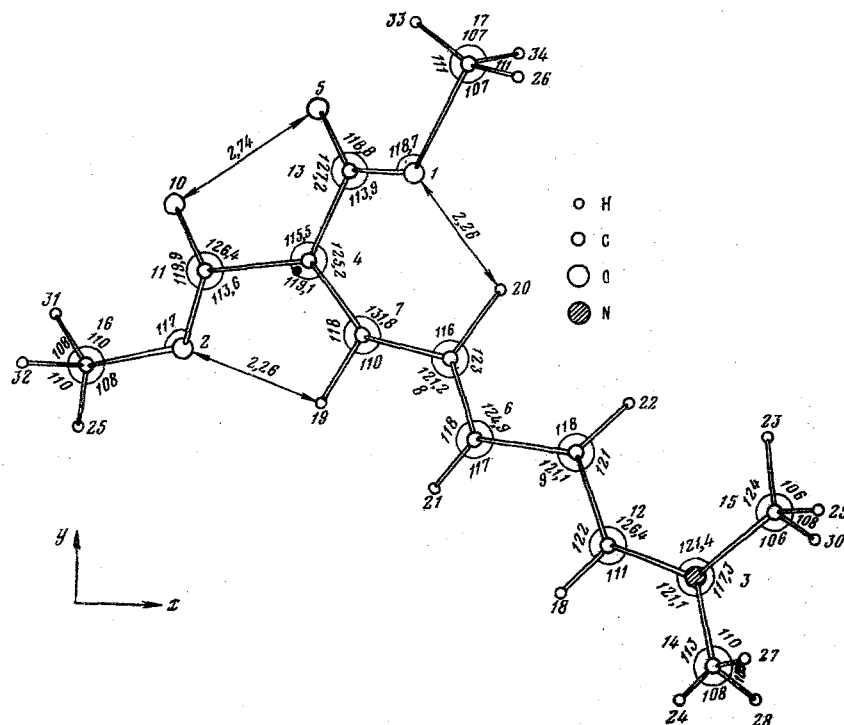


Fig. 1. Molecular geometry of the methyl ester of trans-7-dimethylamino-2-carbomethoxyheptatrienecarboxylic acid.

TABLE 2. Interatomic Distances (Å)

Bond	Bond length	Bond	Bond length	Bond	Bond length
O ¹ -C ¹³	1,333 (4)	C ⁶ -C ⁸	1,372 (5)	C ¹⁴ -H ^{28*}	1,08
O ¹ -C ¹⁷	1,440 (5)	C ⁶ -C ⁹	1,395 (4)	C ¹⁵ -H ^{29*}	1,14
O ² -C ¹¹	1,329 (4)	C ⁶ -H ²¹	1,11	C ¹⁵ -H ^{29*}	1,08
O ² -C ¹⁶	1,434 (4)	C ⁷ -C ⁸	1,405 (4)	C ¹⁵ -H ^{30*}	1,10
N ³ -C ¹²	1,329 (4)	C ⁷ -H ¹⁹	1,08	C ¹⁶ -H ²⁵	1,11
N ³ -C ¹⁴	1,454 (5)	C ⁹ -H ²²	1,10	C ¹⁶ -H ^{31*}	1,10
N ³ -C ¹⁵	1,449 (6)	C ⁹ -H ¹²	1,372 (5)	C ¹⁶ -H ^{32*}	1,08
C ⁴ -C ⁷	1,371 (5)	O ¹⁰ -C ¹¹	1,187 (5)	C ¹⁷ -H ²⁶	1,11
C ⁴ -C ¹¹	1,459 (4)	C ¹² -H ¹⁸	1,04	C ¹⁷ -H ^{33*}	1,09
C ⁴ -C ¹³	1,449 (5)	C ¹⁴ -H ²⁶	1,05	C ¹⁷ -H ^{34*}	1,10
O ⁵ -C ¹³	1,187 (5)	C ¹⁴ -H ^{27*}	1,08		

TABLE 3. Valence Angles (deg)

Fragment	Angle	Fragment	Angle	Fragment	Angle
C ¹³ O ¹ C ¹⁷	118,7 (4)	C ⁶ C ⁹ H ²²	118	N ³ C ¹⁵ H ^{29*}	108
C ¹⁴ O ² C ¹⁶	117,0 (4)	C ¹² C ⁹ H ²²	121	N ³ C ¹⁵ H ^{30*}	106
C ¹² N ³ C ¹⁴	121,1 (4)	O ² C ¹¹ C ⁴	113,6 (4)	H ²³ C ¹⁵ H ^{29*}	106
C ¹² N ³ C ¹⁵	121,5 (3)	O ² C ¹¹ O ¹⁰	119,9 (4)	H ²³ C ¹⁵ H ^{30*}	104
C ¹⁴ N ³ C ¹⁵	117,3 (4)	C ⁴ C ¹¹ O ¹⁰	126,4 (4)	H ²⁹ C ¹⁵ H ^{30*}	108
C ⁷ C ⁴ C ¹¹	119,2 (4)	C ⁹ C ¹² N ³	126,5 (4)	O ² C ¹⁶ H ²⁵	109
C ⁷ C ⁴ C ¹³	125,3 (3)	C ⁹ C ¹² H ¹⁸	122	O ² C ¹⁶ H ^{31*}	110
C ¹¹ C ⁴ C ¹³	115,5 (4)	N ³ C ¹² H ¹⁸	111	O ² C ¹⁶ H ^{32*}	111
C ⁸ C ⁶ C ⁹	124,9 (4)	O ¹ C ¹³ C ⁴	113,9 (4)	H ²⁵ C ¹⁶ H ^{31*}	109
C ⁸ C ⁶ H ²¹	118	O ¹ C ¹³ O ⁵	118,8 (4)	H ²⁵ C ¹⁶ H ^{32*}	110
C ⁹ C ⁶ H ²¹	117	C ⁴ C ¹³ O ⁵	127,3 (3)	H ³¹ C ¹⁶ H ^{32*}	108
C ⁴ C ⁷ C ⁸	131,8 (4)	N ³ C ¹⁴ H ²⁴	113	O ¹ C ¹⁷ H ²⁶	107
C ⁴ C ⁷ H ¹⁹	118	N ³ C ¹⁴ H ^{27*}	110	O ¹ C ¹⁷ H ^{33*}	111
C ⁸ C ⁷ H ¹⁹	110	N ³ C ¹⁴ H ^{28*}	110	O ¹ C ¹⁷ H ^{34*}	110
C ⁷ C ⁸ C ⁶	121,3 (4)	H ²⁴ C ¹⁴ H ^{27*}	104	H ²⁶ C ¹⁷ H ^{33*}	112
C ⁷ C ⁸ H ²⁰	116	H ²⁴ C ¹⁴ H ^{28*}	108	H ²⁶ C ¹⁷ H ^{34*}	111
C ⁶ C ⁸ H ²⁰	123	H ²⁷ C ¹⁴ H ^{28*}	109	H ³³ C ¹⁷ H ^{34*}	107
C ⁶ C ⁹ C ¹²	121,2 (4)	N ³ C ¹⁵ H ²³	124		

TABLE 4. Coefficients for the $Ax + By + Cz = D$ Plane Equations, Projections of the Atoms Out of the Plane, and Angles between the Planes

Plane	Atom	Projection out of the plane, Å	A	B	C	D	Angle between the planes	
							I	IV
I	C ¹¹	-0,0518	2,944	2,635	-10,553	0,795		0°36'
	C ⁴	0,0498						
	C ⁷	0,0253						
	C ⁸	0,0324						
	C ⁶	-0,0044						
	C ⁹	-0,0362						
	C ¹²	-0,0501						
	N	-0,0271						
	C ¹⁴	0,0669						
	C ¹⁵	-0,0048						
II	C ⁴	-0,0027	-3,266	0,016	10,623	0,132	-10°	-9°10'
	C ¹¹	0,0188						
	O ¹⁰	-0,0088						
	O ²	-0,0115						
	C ¹⁶	0,0043						
III	C ⁴	0,0072	5,470	3,759	-8,746	3,365	23°40'	23°58'
	C ¹³	-0,0018						
	O ⁵	-0,0025						
	O ¹	-0,0126						
	C ¹⁷	0,0097						
IV	C ¹³	0,0553	2,953	2,421	-10,577	0,657		
	C ⁴	-0,0013						
	C ⁷	-0,0102						
	C ⁸	-0,0009						
	C ⁶	-0,0204						
	C ⁹	-0,0488						
	C ¹²	-0,0448						
	N	-0,0170						
	C ¹⁴	0,0965						
	C ¹⁵	-0,0084						

the diene of (I) (1.376; 1.408; 1.360 Å), the π -electron system being delocalized to the same extent in each molecule. The geometrical parameters for the COOCH₃ groups differ only slightly. From the practical standpoint, these two groups can be considered as structurally equivalent. The difference in their rotations relative to the triene system (14°) is too small to be considered as evidence of a difference in the degree of conjugation. It has already been pointed out that the difference in angles of rotation is much greater in (I), so much so that only one of the two COOCH₃ groups conjugates with the diene system. Thus the x-ray data shows that an increase in the number of double bonds from two to three makes the bond system conjugation more nearly planar in the triene than in the diene.

The geometrical interaction between the ester oxygen atom (O²) and the H atoms at the CY carbon atoms leads to a pronounced deformation of both the C¹³C⁴C⁷ (125.2°) and the C⁴C⁷C⁸ (131.8°) angles, but the angle of rotation of plane III relative to plane I is still small (24°). The O¹-H²⁰ and O²-H¹⁹ bond lengths are almost identical at 2.26 Å.

The electronic structure of (II) was determined through quantum-chemical calculations, following the self-consistent field MO LCAO method in the CNDO/2 approximation [6-8]. The resulting values of E_{A-B} , a measure of the bond strength [9], and of q , the atomic charge, are given in Table 5.

Values of the experimentally determined C-N bond lengths are compared with the corresponding values of E_{C-N} for (I) and (II) in Table 6. It is obvious that the value of E_{C-N} for the contracted C-N bonds in (I) and (II) is greater in absolute value than E_{C-N} for the normal C-N bond, which is consistent with our understanding of the role played by the unshared electron pair of the nitrogen atom in $p\pi$ conjugation [10].

The triene system differs from the diene system insofar as all three of its double bonds are thermodynamically equivalent. The single bonds are also equivalent here, being almost identical with the bonds met in (I). The electronic structures of the two ester groups are also almost identical.

It can be seen from Table 5 that the molecule of (II) has five reactive nucleophilic centers: O, C(α , γ , ϵ), and N, with the atomic charges falling off in the order: $q_o > q_\alpha > q_\epsilon > q_\gamma > q_N$ (in the diene, $q_o > q_\alpha > q_\gamma > q_N$).

TABLE 5. Two-Center Energies E_{AB} (a.u.)* and Atomic Charges (q)

Bond	E_{AB}	Bond	E_{AB}	Bond	E_{AB}
O ¹ -C ¹³	-1,119	C ⁶ -C ⁸	-1,498	C ¹⁴ -H ^{28*}	-0,755
O ¹ -C ¹⁷	-1,024	C ⁶ -C ⁹	-1,274	C ¹⁵ -H ²³	-0,753
O ² -C ¹¹	-1,121	C ⁶ -H ²¹	-0,741	C ¹⁵ -H ^{29*}	-0,746
O ² -C ¹²	-1,028	C ⁷ -C ⁸	-1,265	C ¹⁵ -H ^{30*}	-0,752
N ³ -C ¹⁴	-1,074	C ⁷ -H ¹⁹	-0,736	C ¹⁶ -H ²⁵	-0,757
N ³ -C ¹⁵	-1,078	C ⁹ -H ²²	-0,766	C ¹⁶ -H ^{31*}	-0,758
C ⁴ -C ⁷	-1,498	C ⁹ -C ¹²	-1,506	C ¹⁶ -H ^{32*}	-0,759
C ⁴ -C ¹¹	-1,173	O ¹⁰ -C ¹¹	-1,606	C ¹⁷ -H ^{33*}	-0,759
C ⁴ -C ¹³	-1,185	C ¹² -H ¹⁸	-0,744	C ¹⁷ -H ^{34*}	-0,760
O ⁵ -C ¹³	-1,607	C ¹⁴ -H ²⁴	-0,752	C ¹⁷ -H ²⁶	-0,759
N ³ -C ¹²	-1,248			C ¹⁴ -H ^{27*}	-0,752

Atom	q	Atom	q	Atom	q	Atom	q
O ¹	-0,253	C ⁹	-0,130	H ¹⁹	-0,017	H ²⁸	0,010
O ²	-0,250	C ¹¹	0,425	H ²⁰	0,030	H ²⁹	-0,001
N ³	-0,095	C ¹²	0,171	H ²¹	-0,015	H ³⁰	-0,008
O ⁵	-0,338	C ¹³	0,429	H ²²	0,016	H ³¹	-0,002
O ¹⁰	-0,339	C ¹⁴	0,084	H ²³	0,014	H ³²	-0,008
C ⁴	-0,176	C ¹⁵	0,086	H ²⁴	0,001	H ³³	0,001
C ⁶	0,103	C ¹⁶	0,135	H ²⁵	-0,012	H ³⁴	-0,011
C ⁷	0,129	C ¹⁷	0,133	H ²⁶	-0,010		
C ⁸	-0,102	H ¹⁸	-0,003	H ²⁷	0,002		

*1 a.u. \approx 625 kcal/mole.TABLE 6. C-N Bond Lengths and the Corresponding Values of E_{C-N}

Bond	Bond length, Å		E_{C-N} , a.u.	
	(I)	(II)	(I)	(II)
C-N (concentrated)	1,338	1,329	-1,247	-1,248
C-N (normal)	1,467	1,454	-1,064	-1,074
The same	1,461	1,449	-1,064	-1,078

The crystal is built up from individual molecules. The interplanar distances are approximately equal to twice the geometric mean of the van der Waals radii.

The authors would like to thank Zh. A. Krasnaya and E. P. Prokof'ev, for having furnished the compounds used here and for having given us valuable advice concerning the interpretation of the results.

CONCLUSIONS

1. The conformation and geometrical parameters of the methyl ester of trans-7-dimethyl-amino-2-carbomethoxyheptatrienecarboxylic acid have been determined.

2. Self-consistent MO LCAO calculations in the CNDO/2 approximation have shown that the double bonds of the triene system are equivalent.

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EVIDENCE OF CONFORMATIONAL ISOMERISM IN THE UV SPECTRA OF
VINYL, β -CHLOROVINYL, AND β,β -DICHLOROVINYL SULFIDES

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UDC 541.62:543.422.6:547.379.131

The effect of conformational isomerism on the conjugation of third period elements with unsaturated systems has been studied repeatedly. UV and IR spectroscopy have been used to investigate the interaction of the S atom with the β,β -dichlorovinyl group in RSCH=CCl₂ compounds, while evidence of the existence of conformational equilibria has been sought in the UV spectra of the unsaturated RSCH=CH₂ sulfides.

The UV spectra of alkyl vinyl sulfides show two absorption bands, one in the neighborhood of 44,000 cm⁻¹ ($\tilde{\nu}_1$) and one in the neighborhood of 41,000 cm⁻¹ ($\tilde{\nu}_2$). The $\tilde{\nu}_2$ band in the methyl vinyl sulfide spectrum has been assigned to a Rydberg type $\pi \rightarrow 4s^*$ transition [1] and the $\tilde{\nu}_1$ band to the $\pi \rightarrow \pi^*$ transition, while the vibrational structure of the short-wave band (two maxima, separated by 1300 cm⁻¹) has been ascribed to a vinyl group stretching vibration of 1300 cm⁻¹ frequency in the first excited electronic state. Comparison of the spectra of ethyl vinyl sulfide and diethyl sulfide has also led to assignment of the long-wave band in the alkyl vinyl sulfide spectra to $\pi \rightarrow \pi^*$ transitions, and the short-wave band to $\sigma \rightarrow \sigma^*$ transitions [2].

Neither of the interpretations is entirely convincing. Assignment of the $\tilde{\nu}_2$ band to a Rydberg transition is not consistent with the fact that the band appears at 41,000 cm⁻¹, transitions of this kind being usually associated with higher energies. Assignment of the $\tilde{\nu}_1$ band to the $\sigma \rightarrow \sigma^*$ transition was based entirely on the similarity of diethyl sulfide and ethyl vinyl sulfide band forms in the 45,000 cm⁻¹ region of the spectrum; the fact that the oscillator strengths of the $\tilde{\nu}_1$ bands in the spectra of these two compounds differ by a factor of 65 [3]. Table 1 is clear indication, however, that the transitions in question are different. The fact is that these assignments were made without considering the possibility that conformation equilibria might be established in these systems.

It is our opinion that both of the absorption bands in the UV spectra of the alkyl vinyl sulfides arise from electronic transitions in the vinylthio group. The short-wave $\tilde{\nu}_1$ band should be assigned to a $\pi \rightarrow \pi^*$ transition leading from an occupied orbital covering the double bond π orbital and the orbital of the S atom unshared electron pair (UEP) of corresponding symmetry, to an antibonding orbital which possibly covers the nearer vacant S orbitals. Transitions of this kind are characteristic of planar conformers. The $\tilde{\nu}_2$ band is to be associated with a nonplanar (gauche) conformer in which the axis of the UEP is not parallel to the axis of the p_z orbital of the nearest C atom. Electronic transitions of the $\tilde{l} \rightarrow a_\pi$ type are met in molecules which are not planar [5]; here \tilde{l} includes the S atom UEP orbital and, to a lesser degree, the vinyl group π orbital, while a_π is a combination of the double bond π^* orbital and the nearest vacant S atom orbitals.

An increase in the size of R brings about a bathochromic shift in both of the absorption bands in the UV spectra of the alkyl vinyl sulfides; the extinction coefficient ratio

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